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MONITORING AND CONTROL OF
SEA WATER COMPOSITION

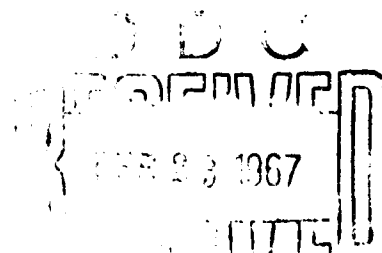
FINAL REPORT

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U.S. Naval Civil Engineering Laboratory
Port Hueneme, California



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FOREWORD

This report was prepared by the Chemical and Structural Products Division of the Von Karman Center, Aerojet-General Corporation, under USN Contract No. NBy 62182. The work was administered under the direction of the Naval Civil Engineering Laboratory, Port Hueneme, with Dr. J. D. Stachiw acting as Program Manager.

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The report covers work conducted from 17 January 1966 through 17 July 1966 and the supplemental period from 11 October 1966 through 13 December 1966. It is submitted in partial fulfillment of the contract and is catalogued by Aerojet-General Corporation as Report No. 3247.

ABSTRACT

This report describes the work carried out in the study and preliminary design of a Sea Water Simulator. The purpose of the device is to approximate for various locales and depths, the sea water chemistry represented by eight chemical parameters: salinity, alkalinity, carbon dioxide, pH, oxygen, hydrogen sulfide, phosphate, and E_h .

A literature search was conducted to elucidate this chemistry and to obtain data quantitatively interrelating these chemical systems and their physical states. A survey was made to compare the characteristics of commercially available control instrumentation and transducers. Based upon the information gathered, a system was then designed. The envisioned system incorporates computer control of both closed-loop and open-loop chemistries. Predicted accuracies for output composition control are reconciled with suggested USNCEL performance specifications.

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I. INTRODUCTION

As interest in the ocean and in the exploration of its depths intensifies, it becomes increasingly vital to formulate and evaluate materials for ocean environment service. Ranking high in importance, the corrosion characteristics of materials need to be determined under the various physical and chemical conditions that may exist at various locales and depths. It is now routine, although often costly, to evaluate test specimens by exposing them in the natural environment. However, the diurnal variations, seasonal fluctuations, and other natural disturbances render it virtually impossible to fix the predominant corrosive factors to the degree available from controlled experimental work. Such studies would be facilitated if the tests could be performed in the laboratory using sea water adjusted to resemble closely the desired environment.

A step in the simulation of the ocean environment has been made in the development of equipment such as the AMF company's Controlled-Environment System. This device variably pressurizes and refrigerates sea water to provide physical conditions found in even the lowest ocean depths. However, simulation of the physical environment alone cannot provide complete test realism, since it is well known that the chemistry of the sea changes with depth. In recognition of this problem, the Naval Civil Engineering Laboratory has generated specifications within which a system for chemical control should operate. Aerojet-General Corporation has been funded to study the feasibility of such a system and to prepare a preliminary design. When coupled with the AMF equipment this envisioned system would thus permit corrosion and other types of testing to be performed in ocean water controlled in terms of both physical and chemical parameters.

The chemical control system would be capable of supplying at a rate of one gpm sea water simulating the ocean environment at pressures from 0 to 20,000 psi and at temperatures from 0 to 20 deg C. This system would be capable of continuously monitoring and controlling the sea-water chemistry with respect to the following parameters and within the indicated ranges and tolerances:

| <u>Parameter</u> | <u>Range</u> | <u>Tolerance</u> |
|------------------------------------|-----------------|------------------|
| Salinity, ppt | 33.0 to 35.0 | 0.01 |
| Alkalinity, meq/l | 0.5 to 3.0 | 0.1 |
| Dissolved free carbon dioxide, ppm | 0 to 50 | 0.5 |
| pH | 6.0 to 9.0 | 0.02 |
| E_h , mv | +2000 to -2000 | 10.0 |
| Dissolved oxygen, ml/l | 0 to saturation | 0.05 |
| Dissolved hydrogen sulfide, ppm | 0 to 50 | 0.5 |
| Phosphate, ppm | 0 to 100 | 0.1 |

Additionally, the system should be corrosion resistant so that it does not contribute heavy-metal ions to uncontaminated sea water in excess of the following concentrations:

| <u>Heavy-metal ion</u> | <u>Concentration, ppm</u> |
|------------------------|---------------------------|
| Copper | 1 |
| Lead | 1 |
| Iron | 5 |
| Nickel | 1 |
| Mercury | 0.05 |
| Vanadium | 0.5 |
| Manganese | 1 |

Practical considerations would also demand that the system be capable of achieving these requirements in long-term, continuous operation. The system should be operable by any qualified engineering technician who would also be capable of providing periodic maintenance adjustments during the normal eight-hours-per-day, five-days-per-week work week.

II. SUMMARY

The program effort falls logically into three tasks constituting a progression from feasibility determination to design generation. The initial task was the clarification and definition of the problems attending the control of sea water chemistry in the complex ocean environment. The second task, an engineering survey, was initiated simultaneously to determine the availability of commercial components for making the required measurements and for fabrication of the simulator system. After the results of these two tasks were screened, the third task, the preliminary design of the simulator, was undertaken and completed. The results of these efforts are summarized below and discussed in detail in the body of this final report.

The first task consisted primarily of a technical survey to clarify the sea water chemistry of interest to this program, as it is affected by changes in temperature and pressure and by the presence of other chemical and biological species. Generally speaking, the available information indicated that each of the eight chemical parameters is affected to some extent by each of the others, and by pressure and temperature changes. The effects are exhibited variously as interactions or interdependencies of the dissolved species, changes in dissociation values, and changes in the solubility parameters of solute gases. Thus it is not possible to consider the eight chemical parameters as simultaneous independent variables.

Tabulated data or equations expressing these effects were then gathered and the overall problem defined in terms of the quantitative relationships operating among the several variables. Existing data were found to be adequate to cover the ranges specified for this program except in some cases where pressure dependence was sparse or lacking for the higher pressures. It was noted, however, that in many cases the most recent data were obtained about 1930; it would thus be desirable to express these dependencies in terms of data acquired by more modern and reliable techniques.

The second task was an engineering survey to determine the current availability of commercial components for the development of a simulator system that would meet the ranges and accuracies initially specified. Approximately 200 companies were contacted for information regarding pumps, tanks, heat exchangers, valves, piping, mixing columns, filters, eductors, transducers, materials of construction, computers, controllers, and other necessary devices. Mechanical components of compatible materials are produced commercially in the required sizes and configurations. Commercial transducers are adequate to make the required temperature, pressure density, flow, and level measurements. Analytical devices are currently marketed to measure each of the eight chemical parameters, but for several the transducers do not provide the specified accuracy and/or the short response time desired (but not indispensable) for this system. Computers required for calculating the interdependent control functions and for generating reference signals will easily provide the needed accuracies, but industrial controllers generally introduce up to a three percent error in the control operation. Certain of these errors can be minimized by the

selection of the proper control mode, but even so it was found necessary to relax the accuracy limits for several of the eight chemical control parameters. The suggested new control ranges and accuracies are as follows:

| <u>Parameter</u> | <u>New Range</u> | <u>New Tolerance</u> |
|------------------------------------|------------------|----------------------|
| Salinity, ppt | no change | 0.035 |
| Alkalinity, meq/l | no change | no change |
| Dissolved free carbon dioxide, ppm | no change | 1.0 |
| pH | no change | 0.03 |
| E_h , mv | +1400 to -1400 | no change |
| Dissolved oxygen, ml/l | no change | 0.15 |
| Dissolved hydrogen sulfide, ppm | no change | 3.0 |
| Phosphate, ppm | no change | 3.0 |

The third task involved the design of a simulator system based upon the findings of the first two tasks. The design is based upon treatment of the sea water stream at 0 deg C as it circulates in a closed loop at a flow rate of 20 gpm. The circulating stream is continuously analyzed and the composition is adjusted by the addition of solutions and by equilibration with proper gas mixtures. The adjusted stream is drawn off from the main stream of the re-circulating loop at one gpm, and is given a final alkalinity and phosphate adjustment prior to delivery to the AMF Controlled-Environment System. As the stream of adjusted water is continuously removed, it is replaced by a fresh input stream of sea water that has been filtered and pretreated to a desired alkalinity and pH. Because of the complexity of the chemistry of the system, a digital process computer is incorporated to calculate the required concentrations based upon selected, set-point values and instantaneous transducer signals, and to provide the rapid updating of reference signals based on these calculations.

As part of the design effort, drawings and specifications were prepared to cover the simulator design and the preliminary component requirements. It is believed that this design, utilizing commercial components, will provide a system capable of giving a one-gpm adjusted stream whose composition is within the ranges and accuracies of the revised specification plan.

Finally, a brief experimental effort was carried out. The purpose of this work was twofold: (1) to demonstrate that the key process effects in the simulator design would produce the results predicted and without deleterious side chemical effects, and (2) that commercially available sensors envisioned as suitable for this design would perform as rated. The first task element resulted in gratifying validation data; the second was frustrated by a lack of loan-equipment availability.

III. SEA WATER CHEMISTRY

The chemistry of sea water is extremely complex because of the high ionic strength and the diversity of ions present. Because of these two factors the sea water system is well buffered with respect to pH (hydrogen ion) and E_h (redox potential) changes. The concentrations of the major species vary only within a limited range - one that is governed by oceanographic, geologic, atmospheric, and climatic factors. Biologically active solutes may fluctuate over a wider range, but these variations are generally cyclic in nature.

Data obtained from the literature and private communications indicate that the concentrations of the eight chemical parameters of interest on this program fall well within the control ranges specified, and in many cases occupy only small portions thereof. Typical values for the Pacific Ocean area or in the vicinity of Port Hueneme are given in Table 1.

The ions and dissolved gases present in sea water react or are capable of reacting and interacting in a variety of ways. The reaction rates and paths, as well as the completeness of the reactions are affected by ionic concentrations, the presence of other species and by the pressure and temperature of the sea water. This discussion is presented to define these interactions and interdependencies. It will, however, be limited to the chemical and physical parameters affecting the design of the simulator system.

A. SALINITY

In 1901 Knudsen defined salinity as "the weight in grammes of the dissolved inorganic matter in 1 kg of sea water, after all bromide and iodide have been replaced by the equivalent amount of chloride, and all carbonate converted to oxide." However, the direct determination of salinity in accordance with this definition proved too difficult and other methods were explored for its measurement. Subsequent comparisons of density, salinity, and chlorinity indicated a reasonably constant relationship between salinity and chlorinity. Chlorinity was defined as the halide concentration in parts per thousand (ppt) by weight measured by the silver nitrate reaction and computed on the assumption that all the halide is chloride. The mathematical expression relating chlorinity to salinity was given as:

$$S = 1.805 Cl + 0.030 \quad (1)$$

where: S = salinity, ppt

Cl = chlorinity, ppt

In 1940 the definition of chlorinity was revised to correct for changes in the accepted atomic weights of silver and chlorine. The revised definition stated:

"The chlorinity is the mass in grammes of pure silver necessary to precipitate the halogens in 328.5322 grammes of sea water."

On the basis of 1963 atomic weights this definition is now in error by 43 ppm.

The salinity of sea water, to within 0.01 ppt, may be expressed as the sum of just twelve of the elements in solution: chlorine, sodium, magnesium, sulfur, calcium, potassium, bromine, carbon, strontium, boron, silicon, and fluorine. Salinity and chlorinity are weight ratios and thus independent of temperature and pressure. In consideration of the chemical parameters of interest on this program, it is seen that of the twelve elements comprising the bulk of the salinity value, only carbon (in its carbonate forms) will be specifically measured and controlled in the simulator system.

The method selected for the determination of salinity in the simulator is based upon the measurement of electrical conductivity. In contrast to the gravimetric procedure, electrical conductivity values are affected by temperature and pressure as well as by carbon dioxide (carbon) concentration.

1. The Salinity Role of Carbon Dioxide

The effect of dissolved free carbon dioxide on the electrical conductance of sea water has been investigated by Park and Weyl (Reference 1) in the pH range of 5.0 to 9.0. Using a sea water sample with a chlorinity of 19.0 and a carbonate alkalinity of 2.6 meq/l, they found that the conductance decreases linearly with an increase in the concentration of dissolved free carbon dioxide at the rate of 0.013 percent per millimole of carbon dioxide per liter (0.013%/mmole CO_2 /l). This corresponds to an 0.0148 percent decrease at 50 ppm CO_2 , or an apparent error of 0.005 ppt at 35 ppt salinity.

These investigators also observed that the CO_2 influence on salinity measurement varied with pH. In the range of 6.5 to 7.5 the conductance varied less than the error of measurement, about 0.003 percent. Above and below this pH range, to pH values of 9.0 and 6.0 respectively, the conductivity error increased to about 0.05 percent. The latter corresponds to an error of about 0.02 ppt at a salinity of 35 ppt. Since the maximum errors are within the limits of accuracy of process-type salinity transducers, it will not be necessary to correct for the effect of carbon dioxide on the measured conductivity.

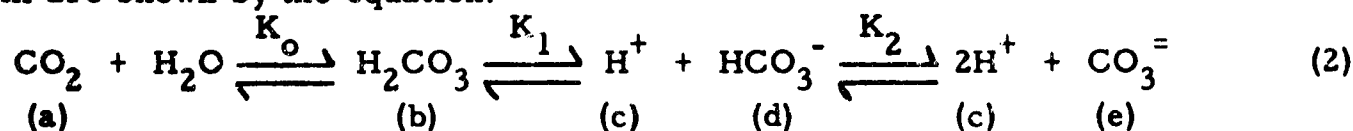
2. Temperature and Pressure Effects

Temperature and pressure both have fairly large effects upon the measured electrical conductivity at a given salinity level. Although numerous papers have been published on this subject, only two of the more recent papers giving detailed treatment of these effects need be mentioned here. Weyl (Reference 2) reviewed and compared the published data of several authors and developed an equation relating conductivity to salinity and temperature. Because of the awkwardness of Weyl's equation, additional equations relating conductivity (K) to the salinity and temperature of sea water were developed on this program. Table 2 gives conductivity-salinity-temperature data and three different equations relating these three parameters. Additionally, the effect of pressure at various temperatures and salinities was published recently by

Schleicher and Bradshaw (Reference 3). Table 3 shows these data and an equation relating the effect of pressure on conductivity at various temperatures and salinities. This latter equation furnishes the multiplicative factor to the equations in the previous table when the effect of pressure must be included. At constant atmospheric pressure the effect of pressure is negligible, and the simpler equation (Table 2) can be employed.

B. ALKALINITY, DISSOLVED FREE CARBON DIOXIDE AND pH

It is virtually impossible to separate the discussion of these three species since the pH, alkalinity, and carbon dioxide concentration are all intimately related. The chemical interactions of the carbon dioxide/carbonate system are shown by the equation:



It should be pointed out, however, that equilibrium does not always exist among these species. In this system the concentration of dissolved free carbon dioxide is indicated by (a), the carbonate alkalinity is the sum of (d) and (e), and the pH is proportional to (c) via the equation:

$$\text{pH} = -\log C_H \quad (3)$$

where: C_H = hydrogen ion concentration, moles/l

or expressed in terms of the hydrogen ion activity:

$$\text{pH} = -\log a_H \quad (4)$$

where: a_H = hydrogen ion activity, moles/l

The relationship among alkalinity, carbon dioxide, and pH values at equilibrium is given by the equation:

$$\text{CA} = 0.022722 C \times d \times \frac{10^{\text{pH}}}{10^{\text{pK}_{L1}}} \left[1.0 + \frac{2.0 \times 10^{\text{pH}}}{10^{\text{pK}_2}} \right] \quad (5)$$

where: CA = carbonate alkalinity, meq/l

C = carbon dioxide concentration, ppm

d = solution density, g/ml

pH = solution pH

$$pK_{L1}' = -\log K_{L1}'$$

K_{L1}' = Lyman's first dissociation constant for carbonic acid

$$pK_2' = -\log K_2'$$

K_2' = Lyman's second dissociation constant for carbonic acid

The three steps of the reaction given in equation (2) are reversible and incomplete. The completeness of the reactions as written is expressed in terms of their thermodynamic equilibrium constants, indicated above as K_o , K_1 , and K_2 .

$$K_o = \frac{a_{H_2CO_3}}{a_{H_2O} \cdot a_{CO_2}} \quad (6)$$

$$K_1 = \frac{a_H \cdot a_{HCO_3}}{a_{H_2CO_3}} \quad (7)$$

$$K_2 = \frac{a_H \cdot a_{CO_3}}{a_{HCO_3}} \quad (8)$$

The use of activities is impractical and therefore new constants have been derived for oceanographic work. In one set the carbonate and bicarbonate values are expressed as concentrations rather than as activities and K_o and K_1 are combined to give two apparent dissociation constants:

$$K_1' = \frac{a_H \cdot C_{HCO_3}}{a_{H_2O} \cdot a_{CO_2}} \quad (9)$$

$$K_2' = \frac{a_H \cdot C_{CO_3}}{a_{HCO_3}} \quad (10)$$

Lyman has prepared a set of values in which the first dissociation constant differs slightly from that given in equation (1). It is related to K_1' as follows:

$$K_{L1}' = K_1' (p_s/p_o) (\alpha_o/\alpha_s) \quad (11)$$

where: p_s = vapor pressure of sea water, atm

p_o = vapor pressure of pure water, atm

α_o = solubility coefficient of CO_2 in pure water, moles/l/atm

α_s = solubility coefficient of CO_2 in sea water, moles/l/atm

It will be noted that Lyman's constants were used in equation (5), above; his values (Reference 4) will be used throughout this report. Tables 4 and 5 give the values for pK_{L1}' and pK_2' respectively, at various temperatures and salinities. Equations derived by project personnel are also given showing the effect of temperature and salinity upon the two dissociation parameters. The table following, Table 6, shows the effect of pressure upon these dissociation values as reported by Harvey (Reference 5) and gives equations derived at Aerojet relating pK_{L1}' and pK_2' to the salinity, temperature, and pressure of the sea water sample.

Reviewing the factors that affect the carbonate alkalinity as determined by equation (5), one observes that it is dependent upon (1) carbon dioxide concentration, (2) solution density, (3) solution pH, and (4) the dissociation values - pK_{L1}' and pK_2' . The dissociation values are, in turn, dependent upon salinity, temperature, and pressure. It should be noted that solution density is also a function of salinity, temperature, and pressure, as is discussed in paragraph III, E, following. Thus the complexity of the chemistry of this system is readily obvious. It is also apparent that for given salinity, temperature, and pressure conditions, the alkalinity, carbon dioxide concentration, and pH are inter-dependent variables. Under such circumstances only two of the latter can operate as independent variables. The third will of necessity be a dependent parameter.

A Fortran IV computer program was prepared to solve equation (5) for representative temperature, salinity, pH, and carbon dioxide conditions. This actual computer program derived for the solution of this equation is reproduced as Figure 1. The data generated are given in Tables 7, 8, and 9. The program was set up so that density, pK_{L1}' and pK_2' values were derived from the temperature and salinity conditions. The carbonate alkalinity was then computed based upon the representative pH and carbon dioxide conditions and calculated values for density, pK_{L1}' and pK_2' . The pressure variable was intentionally omitted from this program.

Referring again to equation (2), it is important to note that the steps in the reaction can be characterized by their velocity constants as well as by their equilibrium constants. In this particular system, step 1 (K_0) is slow and becomes slower with decreasing temperature, whereas steps 2 and 3 (K_1 and K_2) are rapid. The slowness of step 1 imposes severe restrictions on the design of a system that is expected to control accurately and respond rapidly. If the reaction were rapid, for example, the carbonate alkalinity could be controlled through the addition or removal of CO_2 and the adjustment of pH. But because of the slowness of the equilibrium, the chemical factors on each side of the reaction must be controlled. The importance of this factor will be brought out again later in the discussion of the system design.

The foregoing discussion and equations were concerned only with the carbonate alkalinity. The total alkalinity is comprised of the carbonate alkalinity plus other minor amounts of alkalinity contributed by phosphate, sulfide, borate, silicate, selenate, and ammonium ions. In normal surface sea water these minor constituents make up a fairly constant alkalinity of approximately 0.10 meq/l. composed mainly of borate alkalinity. This non-carbonate alkalinity would be increased by the addition of phosphate or hydrogen sulfide, as indicated by the equations:

$$PA = \frac{P \times d}{95} \left[1.0 + \frac{10^{-7.125}}{10^{-\text{pH}} + 10^{-7.125}} \right] \quad (12)$$

where: PA = phosphate alkalinity, meq/l
P = phosphate concentration, ppm
d = solution density, g/ml

$$\text{and } SA = \frac{S \times d}{34} \left[\frac{10^{-7.041}}{10^{-\text{pH}} + 10^{-7.041}} \right] \quad (13)$$

where: SA = sulfide alkalinity, meq/l
S = hydrogen sulfide concentration, ppm
d = solution density, g/ml

As examination of these equations for representative pH values at the desired maximum phosphate (100 ppm) and hydrogen sulfide (50 ppm) control values indicate the possible magnitude of their contributions. At a pH of 6.0 the phosphate alkalinity would be approximately 1.2 meq/l and the sulfide alkalinity would be approximately 0.15 meq/l, whereas at a pH of 9.0, the

phosphate and sulfide alkalinities would be respectively 2.2 and 1.5 meq/l. Thus their contributions cannot necessarily be neglected and the total alkalinity (TA) would properly be expressed by the equation:

$$TA = CA + PA + SA + 0.10 \quad (14)$$

The solubility of carbon dioxide in sea water is considerably greater than that of oxygen or nitrogen because of its chemical interaction. If, however, account is taken only of the dissolved carbon dioxide as such, Henry's law is obeyed. In pure water the concentration is given by:

$$C_{CO_2} = P_{CO_2} \cdot \alpha_o \quad (15)$$

and in sea water:

$$C_{CO_2} = P_{CO_2} \cdot \alpha_s \quad (16)$$

where: C_{CO_2} = carbon dioxide concentration, moles/l

P_{CO_2} = applied pressure of carbon dioxide, atm

α_o, α_s = solubility coefficients, moles/l/atm

The applied pressure has a linear effect upon the carbon dioxide solubility, but the solubility coefficient, α_s , is further affected by the temperature and salinity of the sea water. This relationship, determined by Bohr, was taken from Reference 4 and is shown in Table 10.

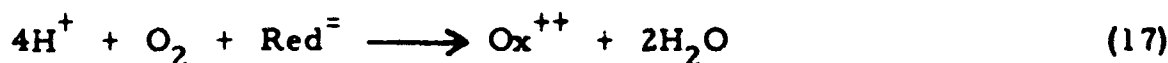
In summary, it will be noted that among the chemical and physical parameters of interest in the simulator design, there is a marked interaction involving the alkalinity-carbon dioxide-pH system. In addition to reacting among themselves, they are affected by the salinity, temperature, and pressure of the solution in which they interact; alkalinity is also increased by the addition of phosphate or hydrogen sulfide in proportion to the pH of the solution.

The factors discussed above reveal that, within the control ranges, only discrete, compatible combinations of the chemical and physical variables can be employed to effect a resultant that in all respects falls within the specified limits. For example, it will not be possible to obtain the minimum alkalinity (0.5 meq/l) at a high pH in the presence of high phosphate or high hydrogen sulfide concentrations. Similarly the data in Tables 7, 8, and 9 reveal that it would be impossible to remain within the specified alkalinity range while maintaining a high pH and a high carbon dioxide concentration. These and other similar factors must be taken into account in the selection of operating conditions.

C. DISSOLVED OXYGEN, DISSOLVED HYDROGEN SULFIDE, AND E_h

The redox potential (E_h) of sea water is determined primarily by the concentration of dissolved oxygen or dissolved hydrogen sulfide. Roughly speaking, positive redox potentials correspond to the presence of dissolved oxygen, whereas negative values indicate a reducing medium such as exists in the presence of dissolved hydrogen sulfide. The progression from positive to negative values corresponds roughly to increases in depth. This is shown in the data of Table 11 taken from Riley (Reference 4). The data also indicate that the sensitivity of the redox potential to changes in oxygen or hydrogen sulfide concentrations is greatest in the transition region where the concentrations of both are low.

The oxygen in sea water may come from the atmosphere or be generated in photosynthetic processes. It is consumed by respiration (biochemical) and by chemical reactions. The possible chemical reactions include oxidation of organic matter and the oxidation of hydrogen sulfide or other dissolved inorganic substances. The chemical reactions may be written in the general form:



which shows that the reduced form (Red^-) is oxidized to the oxidized form (Ox^{++}), and oxygen is reduced to water.

The redox potential of this reaction is expressed by the Nernst equation:

$$E = E_o - \frac{RT}{nF} \ln L \quad (18)$$

$$\text{or } E = E_o - \frac{0.0001984 T}{n} \log L \quad (19)$$

where: E = half-cell potential, volts

E_o = standard potential of the half-cell, volts

T = temperature, deg C

n = number of electrons involved per mole of reactant

$$L = \frac{(Ox^{++})}{(Red^-)} = \frac{(H^+)^4 (O_2)}{(H_2O)^2}$$

In the case of L , the values in parentheses denote concentrations of the indicated species.

In the measurement situation the redox potential is determined by measuring the potential of the (predominant) half-reaction versus a reference electrode having a potential, E_{ref} . The E_h value for sea water containing dissolved oxygen may, therefore, be expressed by the equation:

$$E_h = E_{ref} - E_o + \frac{0.0001984 T}{n} \log \frac{(H^+)^4 (O_2)}{(H_2O)^2} \quad (20)$$

It will be noted that this equation shows the interdependence between the dissolved oxygen concentration and E_h . It also shows that temperature and pH (H^+) have an effect upon the measured value of E_h ; however, in most cases the effect of these two parameters will be small.

The coexistence of dissolved oxygen and hydrogen sulfide is apparently not a thermodynamically stable situation. Ostlund and Alexander (Reference 6) investigated the rate of oxidation of sulfide in sea water at 25 deg C. They found that if there is a large excess of oxygen or a good supply from convection, the reaction between oxygen and sulfide ion may be treated as a first-order reaction. At an oxygen concentration of 5 ml/l the rate constant was approximately 0.04/min. and the half-life of sulfide was about 17 minutes. They suggested that where diffusion of one or both reactants is required to obtain contact, steady-state concentrations may be established. Indications are that the reaction proceeds according to the equation:



As both theoretical and practical evidence indicate that the two species will not remain together in substantial concentrations for any reasonable length of time, redox potential is predicated on the concentration of dissolved oxygen or hydrogen sulfide, but not both.

The saturation concentration (upper limit of solubility) of oxygen in sea water is established by the temperature and salinity of the sea water system. Thermodynamic calculations indicate that the saturation solubility of oxygen in sea water is relatively unaffected by pressure. The solubility at various temperatures and chlorinities (salinities), as determined by Fox (Reference 7), is given in Table 12. This table also contains an equation that fits the data. The equation expresses the solubility of oxygen in ml/l at NTP in sea water equilibrated with dry air at a total pressure of 760 torr. Later values obtained by Truesdale, Downing, and Lowden (Reference 8) are somewhat lower than those of Fox. Recent experimental work by Montgomery, Thom, and Cockburn (Reference 9) gives results that are in fair agreement with those of Fox and thus his values will be used.

Ostlund and Alexander (Reference 6) state that, "At the pH of sea water, 8.2, about 95 percent of the sulfur is present as HS^- ." Clearly then, if a hydrogen sulfide concentration of 50 ppm is to be maintained, the bisulfide (HS^-) concentration will have to be approximately 950 ppm (.028 molar). More realistically, it is taken that the upper limit of 50 ppm will, in solution, be the combined hydrogen sulfide and bisulfide concentrations.

D. PHOSPHATE

The dissolved phosphate in sea water is evidently present as the orthophosphate, primarily as H_2PO_4^- and HPO_4^{2-} . The average phosphate concentration is approximately 0.2 ppm, although in the uppermost 100 meters or so the concentration is usually a good deal less because of the biological processes that consume it. In the simulator system the factor of primary concern, aside from the interference of phosphate with alkalinity as noted previously, would be the biological removal of added phosphate. Kuenzler, Guillard, and Corwin (Reference 10) have described a procedure for the preparation of phosphate-free sea water for reagent blanks by brief contact with phosphorus-deficient diatoms, *P. tricornutum*. Under the conditions they used, more than 97 percent of the phosphate was removed in 2 to 3 hours. Since sea water normally contains less than one ppm of phosphate and the simulator specification calls for the addition of up to 100 ppm, if phosphate-consuming microorganisms are present they might thrive on the high excess and make it difficult or impossible to maintain the desired concentration.

E. DENSITY

The relationship of changing physical and chemical conditions to the density of sea water bears on the design problem at hand. In the case of parametrically expressed weight ratios (salinity, carbon dioxide, hydrogen sulfide, and phosphate), simple density variations brought about by systemic changes in temperature and pressure have no effect. However, density changes can have a significant effect in cases of weight/volume, volume/volume (oxygen), or equivalent/volume (alkalinity) ratios. Sea water density is a function of salinity, pressure and temperature. Typical values of density as a function of temperature and salinity are given in Table 13 along with an equation derived at Aerojet relating density to these parameters. The data of Newton and Kennedy (Reference 11) given in Table 14 also includes the effect of pressure. The data are given as specific volume, the reciprocal of density. The equation given in the same table relating these parameters is more generally applicable than the one in Table 13, but the equation in the latter table is more convenient to use at constant atmospheric pressure, where the effect of pressure may be neglected.

IV. TRANSDUCER REVIEW

In screening transducers for potential application to the simulator design, consideration was given only to automatic methods of measurement. As in any process control system, in-line transducers were favored and are suggested for use in the simulator design, wherever possible. Acceptable in-line transducers were not found for several chemical measurements, which dictated that off-line automatic or repetitive-type analysis procedures be adopted. High priority was given to high accuracy and rapid response.

The sections that follow review the various procedures known to be commercially adapted in hardware form and make recommendations for acceptable transducer types for each analysis. Transducers for the measurement of pressure, temperature, flow, level, and density are not reviewed here, since a wide variety of devices meeting the requirements of this system have been commercially available for many years.

A. SALINITY

Several physical methods have been considered by oceanographers for the determination of salinity. Of the four popular approaches - conductivity, refractive index, sound velocity, and density - each is temperature and pressure sensitive. However, most commercial salinometers are based upon the measurement of refractive index or conductivity. The latter technique is preferred by most workers, as it probably offers the highest ultimate accuracy.

1. Refractive Index

The use of refractive index for the determination of salinity apparently has not gained widespread use among oceanographers in spite of the fact that the temperature sensitivity of this technique is much lower than that of conductivity measurements. Sample temperature can vary by ± 2 deg C without producing a significant error in the salinity value derived by refractive index. For a one ppt increase in salinity, the refractive index increases by approximately 0.0002. In order to achieve a sensitivity of 0.05 ppt, one would have to measure the refractive index precisely to 0.00001. Since the best commercial in-line refractometer has a sensitivity of about 0.0002 refractive index units, these process instruments are capable of monitoring salinity values to only about one ppt.

2. Conductivity

A large selection of instruments are commercially available for determining salinity conductimetrically. The two basic types involve: (1) the measurement of d-c conductivity between two electrodes (usually platinum), and (2) the determination of a-c conductivity between two coils inductively coupled by the sea water medium. The two techniques appear to provide equivalent accuracies. The inductive coupling approach offers the advantages that (1) there is no polarization problem at the electrodes, and (2) the metal

electrodes do not come into direct contact with the sea water, and thus are relatively unaffected by fouling and corrosion. Inductively coupled, conductivity-type transducers are recommended for use in this design.

As the conductivity measurements are pressure and temperature sensitive, the accuracy obtained in salinity determinations will depend upon the degree of compensation of the transducer as well as its own intrinsic accuracy. A temperature change of 0.001 deg C produces a change in conductivity of one part in 40,000 at 35 ppt salinity. In order to obtain an accuracy of 0.01 ppt, the temperature would have to be controlled to within approximately 0.01 deg C. Commercial sensors, temperature-compensated over a range of 0 to 30 deg C and suitable for in-line installation, furnishing accuracies of 0.03 ppt are available (quality laboratory devices give accuracies of 0.003 ppt). Pressure (to 6000 meters) and temperature compensated sensors are also available that provide an accuracy of 0.03 ppt.

B. ALKALINITY

As far as is known there is no true in-line alkalinity sensor. The continuous analyzers available are simply devices that have automated the colorimetric or titrimetric procedure for the alkalinity determination. Sea water is removed from the process line by means of a sampling tee and directed to the automatic analyzer. Some devices mix sample and reagents and measure alkalinity colorimetrically, while others titrate to an acidimetric end point. In each case a signal proportional to alkalinity is produced. These processes may give repetitive or continuous analyses of the stream.

The best accuracy of such devices is on the order of two percent and may typically be three percent. The response time, determined by the length of the sample-and-measure cycle, is typically 3 to 5 minutes. Although these analyzers do not possess the accuracy or response-time characteristics that are desired, they must be incorporated in the simulator design because no other alkalinity-measuring technique appears to be currently available.

C. DISSOLVED FREE CARBON DIOXIDE

Carbon dioxide is commonly measured in process streams by gas chromatographic (GC) or non-dispersive infrared (NDIR) techniques. Recently one company introduced a "carbon-dioxide electrode." These three techniques for carbon dioxide measurement are reviewed here with a view to their applicability to the present analysis situation. The NDIR approach is recommended in this design.

1. Carbon Dioxide Electrode

In recent months Beckman Instruments has developed an electrode for the measurement of carbon dioxide concentrations. The sensing element consists of a glass-calomel electrode pair immersed in an electrolyte that is one molar in potassium chloride and one-hundredth molar in sodium bicarbonate. The electrolyte is separated from the process fluid by means of a

gas-permeable membrane. Carbon dioxide in the process stream diffuses through the membrane and reacts with the electrolyte, changing its pH. The pH change, sensed by the glass-calomel electrode pair, is proportional to the carbon dioxide concentration in the sample stream (which may be either a liquid or gas) from 0 to 100 percent. The manufacturer reports that a ten-fold change in the carbon dioxide concentration gives a 55 to 57 mv signal change. The optimum sensitivity is in the range from 1.3 to 100 percent carbon dioxide (gas phase).

One major problem with this sensor is the long response time. In the 1.3-to-100 percent range the response time is approximately 10 to 15 minutes. Below 1.3 percent the response time may be as long as 25 to 30 minutes. This slow response arises, not from mass transfer rate through the membrane, but because of the slow rate of hydration of carbon dioxide to form carbonic acid. This is the same slow reaction discussed earlier and indicated in equation (2) as K_o . This velocity constant is temperature dependent, so that the response time of the carbon dioxide sensor will also be temperature dependent. Inasmuch as the carbon dioxide levels operating in the simulator will be well below one percent, the carbon dioxide electrode would not be acceptable for use.

2. Gas Chromatography

Recent interest in the rapid analysis of dissolved gases in sea water has led to the development of specialized gas chromatographs for this purpose. One commercial gas analyzer is based upon the technique described by Linnenbom, Swinnerton, and Cheek (Reference 12) of the U.S. Naval Research Laboratory (USNRL) for the determination of dissolved oxygen, nitrogen, and potentially carbon dioxide. Williams and Miller (Reference 13), also of the USNRL, have described an instrument for the analysis of oxygen, nitrogen, and carbon dioxide in sea water. Both groups of workers noted that their methods may be adaptable for hydrogen sulfide determination. This research has established the feasibility of gas chromatographic methods for the determination of dissolved gases, as has been amply demonstrated by the U.S. Naval Oceanographic Office both at sea, and in the laboratory.

The actual analysis involves first the separation of dissolved gases from the sea water by stripping the latter with a carrier gas. After any necessary gas treatment such as drying, the remaining gases are separated into components, which are then detected by the gas chromatograph. Two different stripping methods are utilized in the two approaches mentioned above. The first, using a glass column with a fritted-glass disk in the bottom, achieves separation by bubbling the purge gas up through the sea water. The second employs a multiple spinning-disk stripper to transfer dissolved gases from the liquid to the purge gas. In each case the purge gas, helium, serves as the carrier gas for the separation step in the gas chromatograph. Both techniques employ a Molecular Sieve packing in the separating column and thermal conductivity detectors.

In general a Molecular Sieve column will separate nitrogen and oxygen, but will not elute peaks for carbon dioxide, hydrogen sulfide, and certain other dissolved-gas components. The determination of carbon dioxide, for example, requires a special second column.

Although the two reports cited here do not indicate specifically the sensitivity to carbon dioxide, this value can be estimated from the sensitivity to oxygen. The latter states that in the use of a five-ml sea water sample, the technique can sense differences in the oxygen or nitrogen content as low as 0.02 ml/l. Assuming saturation values for oxygen of 10 ml/l, this represents a sensitivity of 0.2 percent. However, the typical accuracy for an analysis by gas chromatography is not better than 2 percent.

The characteristic cycle time for an analysis by gas chromatography is 4 to 5 minutes. This is one of the primary factors operating against its use in this application.

3. Non-dispersive Infrared

The NDIR technique has been applied quite effectively to the determination of carbon dioxide and other infrared-absorbing gases in process streams. The sample gas is passed continuously through a sample cell and the intensity of its infrared absorbance is compared to that of a non-absorbing gas in a reference cell. The detector cell, sensitized to carbon dioxide, compares the intensity of radiation received from sample and reference cell and generates a signal proportional to the carbon dioxide content of the sample stream.

Several factors influence the analyzer readings, including (1) the composition of the sample gas, (2) the total pressure of the sample gas, and (3) the temperature of the system. There is no problem if carbon dioxide is the only infrared-absorbing gas, but if other compounds are present that absorb significantly in any of the principal regions of the carbon dioxide spectrum, they must be removed. In the analysis of sea water, drying the stripped gas to remove moisture is normally adequate treatment. Fluctuations in temperature and pressure produce corresponding changes in sample volume that results in apparent variations in concentrations.

Although the readout from a NDIR analyzer is continuous, a finite time is required to sense a change in the carbon dioxide content of sea water. This time lag results not only from the stripping and drying operations, but from the delay occasioned as the prepared sample gas displaces the gas already present in the cell of the analyzer. While sensitivity requirements dictate a long-path cell, a short response time demands a short-path (small volume) cell. Optimization will involve a trade-off between these two factors.

One of the earliest and most accurate NDIR analyzers was described by Smith (Reference 14). Several of these instruments have been used in oceanographic laboratories with good results. Takahashi (Reference 15) found that in laboratory use the instrument provided continuous measurements at an accuracy of 0.3 ppm at the 100 ppm level. Unfortunately, an instrument of this specific design is no longer commercially available.

At the present time there are four or five companies offering NDIR analyzers for process type applications. These instruments provide accuracies

of one or two percent. The response time of the instrument is approximately 0.5 sec, but the response time of the entire carbon dioxide sensing step is on the order of one to two minutes because of the intermediate gas processes just mentioned. Nonetheless, the accuracy and response time of NDIR are still better than those obtainable by gas chromatography.

D. pH

The pH of sea water may be determined conveniently using the glass-calomel electrode system. Commercial, in-line devices are available covering the pH range from 0 to 11 with an accuracy of 0.02 pH unit and with a 24-hour stability of 0.01 pH unit. The response time is on the order of 10 seconds. Thus the accurate measurement of pH should be no problem.

E. E_h

The redox potential (E_h) of sea water and other aqueous solutions is commonly measured by means of a platinum-calomel electrode pair. Electrode assemblies for in-line monitoring are commercially available giving accuracies of ± 10 mv over the standard range of ± 1400 to -1400 mv. It should be noted that the redox potential of sea water normally falls within the range from $+400$ to -150 mv. The maximum range that could be obtained in sea water would probably be ± 1300 to -1000 mv, where water or dissolved species would be respectively oxidized and reduced. The suggested specification range of ± 2000 to -2000 is unnecessarily broad. Because the platinum-calomel electrode pair provides a response time of approximately 10 sec, available commercial devices would appear to offer the required accuracy over an adequate range.

F. DISSOLVED OXYGEN

Many oxygen sensors have been developed for process applications. The techniques employed include catalytic oxidation of hydrogen, measurement of oxygen paramagnetism, the electrochemical reaction of oxygen, and various automated colorimetric methods. Then, too, dissolved oxygen may be stripped from the solution and determined by gas chromatography, as discussed in paragraph IV. B, above. Devices based upon the electrochemical principle are best suited to the present design, as they are commercially available as in-line sensors, provide short response times, and offer accuracies equivalent to other techniques.

In the electrochemical sensors, the oxygen-sensitive electrodes are separated from the sample stream by a selectively permeable membrane of polyethylene or polytetrafluoroethylene. Oxygen diffusing through this membrane reacts electrochemically at the electrodes by a galvanic or coulometric process. In the galvanic cell the electrochemical reduction of oxygen produces a potential in proportion to its concentration. In the coulometric cell an appropriate voltage applied to the electrodes of the cell cause the electrochemical reduction of the oxygen at the cathode and, in turn, produces a current in proportion to the oxygen concentration. The response times of these dissolved oxygen sensors is approximately 10 sec., and the accuracy is normally one percent of full scale at constant temperature.

When the sample temperature varies, temperature compensation can be provided, although at a considerable sacrifice in accuracy. By operating the simulator system at constant temperature, it should be possible to measure oxygen concentration to an accuracy of ± 0.1 to 0.2 ml/l over the range up to saturation.

G. DISSOLVED HYDROGEN SULFIDE

Several sulfide-sensitive electrodes have been evaluated by manufacturers for commercial applications. These metal/metal sulfide couples include: silver/silver sulfide, mercury/mercury sulfide, and lead/lead sulfide. Evidently these electrode systems exhibit irreversibility and drift problems, and have not come into general use for the measurement of hydrogen sulfide in either solution or the gas phase.

The USNRL gas chromatographic method described previously in paragraph IV. B. could perhaps be developed for hydrogen sulfide determination, but insofar as is known, there are no available commercial devices based on this technique.

Colorimetric gas analyzers have been developed for the measurement of hydrogen sulfide over concentration ranges as low as 0 to 8 ppm. The hydrogen sulfide is absorbed from the gas phase by a liquid reagent to produce a colored species that is measured colorimetrically. Because a gas sample is required, the first step necessarily involves the separation of the dissolved hydrogen sulfide from sea water by means of an inert stripping gas. The colorimetric procedure requires approximately 10 minutes and gives an accuracy of approximately three percent of full scale. Although the accuracy and response time offered here do not meet those desired, the technique would perhaps be acceptable if the response time could be brought more in line with the present design requirements.

The analyzer recommended for inclusion in the simulator system is a coulometric gas analyzer that is available commercially for the determination of hydrogen sulfide and other sulfur-containing compounds in gas streams. The hydrogen sulfide, stripped from sea water by means of an inert carrier gas such as nitrogen, is absorbed in a coulometric titration cell where it is continuously reacted with electrolytically generated bromine. The net generating current required to maintain a slight excess of bromine is directly proportional to the hydrogen sulfide concentration. The response time of the instrument is 30 seconds, to which must be added the lag time of the sample line of approximately another 30 seconds. This electrolytic titrator is sensitive to 0.08 ppm of hydrogen sulfide, but provides a measurement accuracy of only 5 percent.

H. PHOSPHATE

Direct-reading electrodes for phosphate measurement have recently been developed. The electrode features a phosphate-sensitive membrane which unfortunately, also responds to large concentrations of chloride and sulfate. The manufacturer claims that the electrode has a specificity of one ppm phosphate in 40 ppm chloride or in 100 ppm sulfate. Thus it is probable that in sea water the electrode would be totally insensitive to phosphate.

It appears that the only device for continuous phosphate analysis is, as in the case of alkalinity, an automatic analyzer. The colorimetric procedure used in the laboratory for phosphate determination has been automated, furnishing a response time of three to five minutes. The accuracy of the analysis falls in the range of 2 to 5 percent. Although this does not meet the 0.1 ppm accuracy originally specified (at the 100 ppm level), it is the best currently offered device adaptable to process control.

V. SUMMARY OF TRANSDUCER RANGES AND ACCURACIES

In view of the ranges and accuracies available in commercial systems for process stream applications, the transducer specifications summarized below reflect what is believed to be the best available. The transducer specifications are compared with the original specifications suggested for the ultimate system. This list includes only the transducer accuracy and does not factor in the accuracy contributions of other process control parameters, which will be considered in later sections.

| <u>Chemical Parameter</u> | <u>Tentative</u> | <u>Transducer</u> |
|---------------------------|-----------------------------|----------------------------|
| Salinity, ppt | 33.0 to 35.0, ± 0.01 | 33.0 to 35.0, ± 0.03 |
| Alkalinity, meq/l | 0.5 to 3.0, ± 0.1 | 0.5 to 3.0, ± 0.06 |
| Carbon Dioxide, ppm | 0 to 50, ± 0.5 | 0 to 50, ± 0.5 |
| pH | 6.0 to 9.0, ± 0.02 | 6.0 to 9.0, ± 0.02 |
| E_h , mv | +2000 to -2000, ± 10 | +1400 to -1400, ± 10 |
| Oxygen, ml/l | 0 to saturation, ± 0.05 | 0 to saturation, ± 0.2 |
| Hydrogen Sulfide, ppm | 0 to 50, ± 0.5 | 0 to 50, ± 2.5 |
| Phosphate, ppm | 0 to 100, ± 0.1 | 0 to 100, ± 2 |

VI. MATERIALS OF CONSTRUCTION

In the construction of the simulator, non-metals are preferred wherever their use is practical. However, it is realized that metals will have to be used in contact with sea water in certain components. This section briefly discusses and lists some of the metals and non-metals that are reported to possess acceptable corrosion resistance in sea water service. The list includes only the more common materials, since cost considerations would often rule out the use of exotic materials.

A. METALS

The corrosion of metals in sea water has been reviewed by Fink (Reference 16). He notes that, "The chemistry of sea water is complex and much more information needs to be developed. Many materials behave unpredictably in sea water, particularly when incorporated into actual designs." He also stresses that corrosion is electrochemical in nature, pointing up the need for care in the use of dissimilar metals in the system. Although this report deals specifically with the problems encountered in desalting plants, the information presented indicates that titanium, Monel, Inconel, and Hastelloy C would be acceptable for use in components that would come into contact with sea water in the simulator. Titanium should normally not be coupled with most other metals in the presence of sea water because the attack upon the other metal is greatly increased. Titanium is the preferred metal for all parts in this system in contact with sea water.

B. NON-METALS

Nearly all plastics, polymers, and rubbers are chemically compatible with sea water. The two basic problems encountered are (1) the growth of molds and microorganisms on certain surfaces, and (2) flow under stress. Thus acceptable non-metals should possess the following characteristics:

- No added plasticizer:- Plasticizers tend to promote or support the growth of molds and microorganisms.
- Low moisture absorption:- The absorption of moisture causes dimensional changes in polymers.
- Low cold flow:- Polymers with high cold-flow yield more readily under stress.

The cold flow problems can be minimized by designing the system so that the weight distribution and location of parts results in minimum stress.

In general the halogenated (chlorinated or fluorinated) polymers yield better corrosion resistance than do the non-halogenated materials. Thus chlorinated polyethers, polyvinylchloride, polytetrafluoroethylene, and other halogenated polymers are recommended for first consideration as materials of construction, keeping in mind their cold-flow characteristics. Polyethylene and polypropylene are also acceptable materials of construction, as are Pyrex glass and glass-reinforced plastics.

VII. DESIGN

The design of the Sea Water Simulator is based upon the chemistry described in Section III and upon the availability and characteristics of transducers reviewed in Section IV. The design is set forth in Aerojet Drawing No. 099562, Sheets 1 through 12, reproduced in this report in reduced format as Figures 2 through 13, inclusively. A preliminary specification, AGC-10545, covering the requirements of the components of the simulator is contained in this final report as an Appendix.

This section provides a description of the design and an amplification of details shown in the drawing. The individual sheets present functional and detailed representations of the process flow plan and the computer/controller. The content of the twelve sheets of the drawing is indicated by the titles:

| <u>Sheet</u> | <u>Figure</u> | <u>Title</u> |
|--------------|---------------|---|
| 1 | 2 | Index |
| 2 | 3 | Equipment List |
| 3 | 4 | Instrumentation Code |
| 4 | 5 | Identification of Physical and Chemical Parameters |
| 5 | 6 | Process Flow Plan |
| 6 | 7 | Functional Block Diagram of the Computer/Controller |
| 7 | 8 | Functional Details of the Digital Computer |
| 8 | 9 | Computer Corrections |
| 9 | 10 | Computer Corrections |
| 10 | 11 | Block Diagrams of the Analog Controllers |
| 11 | 12 | Block Diagrams of the Analog Controllers |
| 12 | 13 | Block Diagrams of the Analog Controllers |

A. OPERATIONAL DESCRIPTION

The Sea Water Simulator is designed to provide a one gpm flow of adjusted sea water at 0 deg C and at less than 50 psig. The process flow plan for the system is given in Figure 6 (Sheet 5). The incoming (raw) sea water stream is obtained from an existing NCEL facility, which takes sea water from a point some 1000 ft offshore. This raw stream, at ambient temperature, is pumped by the simulator system through two filters in series to remove sand, suspended particles, and microorganisms, thus effectively sterilizing the raw feed stream. The filtered sea water is then carried to pretreatment tanks for a preliminary adjustment of alkalinity and pH. Just prior to entering the first tank, the alkalinity of the filtered stream is periodically measured and, if the alkalinity is above that desired in the final output stream, a controller system

is activated causing hydrochloric acid to be continuously added to bring the pH of the solution in the first tank down to 5. Simultaneously, air or nitrogen gas is bubbled through the solution to strip the sea water of the carbon dioxide liberated from the carbonate system by the acid addition. The choice of air or nitrogen depends upon whether oxygen or hydrogen sulfide is to occur in the final output stream. If, on the other hand, the alkalinity of the filtered input stream is at or below that required in the output stream, acid will be continuously added to the first tank, if required, but only to adjust the pH of the incoming stream downward and to within 0.1 unit of the pH required in the output stream. In the second tank, if required, the pH is adjusted upward by the continuous addition of sodium hydroxide solution to bring the pH to within 0.1 unit of the desired final pH. These pH adjustments are preliminary and aimed at simplifying the process chemistry that follows.

After this pretreatment the stream is pumped into a recirculating loop via a heat exchanger that lowers the sea water temperature to approximately 0 deg C. Within this closed loop, the sea water stream is circulated at a rate of 20 gpm, during which time the stream is constantly analyzed, adjusted by the addition of solutions, equilibrated with a gas mixture, and maintained at a temperature of zero to one deg C. In completing one cycle around the loop, the sea water receives, as required, sodium bicarbonate solution (alkalinity adjustment), concentrated sea water or distilled water (salinity adjustment), and additional sodium hydroxide solution or hydrochloric acid solution (final pH adjustment). The stream is passed through a heat exchanger and then through a counter-current mixer in which the liquid stream is equilibrated with a gas stream. The gas mixture, containing oxygen, carbon dioxide, or hydrogen sulfide, as required, has a composition such that the concentration in the solution phase is brought to that desired in the final output stream. As the sea water stream exits from the mixing column, it is again passed through a heat exchanger and then pumped through the analyzer section. This section, consisting of duplicate parallel lines to facilitate servicing and calibration during extended testing, contains in-line transducers or sampling tees to bypass stream samples to analyzers. Here the analysis of salinity, alkalinity, dissolved free carbon dioxide, pH, E_h , dissolved oxygen, dissolved hydrogen sulfide, phosphate, temperature, and pressure are accomplished. On leaving the analyzer section, the stream continues around the loop. A portion of this adjusted sea water is removed at a rate of one gpm, while the remainder acquires a one gpm input stream of pretreated sea water prior to recycle.

On leaving the loop, the one gpm stream of chemically adjusted sea water passes through an eductor and then to another heat exchange stage. The required amount of phosphate solution and sodium bicarbonate solution (final alkalinity adjustment) are added at the eductor to create the concentrations desired. The eductor also provides mixing of the merging streams. The final heat exchanger brings the temperature of the adjusted stream to the same temperature as required in the AMF System. This sea water stream is now adjusted to the final concentrations and conditions, except for those brought about by pressurization. For the reasons outlined below, it must be injected into the AMF System without delay.

The design incorporates a computer/controller to handle the complex chemistry of sea water. A small digital computer is incorporated to calculate the interactions among salinity, alkalinity, carbon dioxide, pH, oxygen, hydrogen sulfide, phosphate, temperature, and pressure; these are indicated in Figure 8 (Sheet 7) and shown in detail in Figures 9 (Sheet 8) and 10 (Sheet 9). The actual control of these and the other functions, such as the pretreatment steps, level control, etc., is handled by analog controllers. Their function is indicated in the block diagrams of Figures 11 through 13. The combined digital-analog system is designed to give the optimum accuracy through the use of proportional analog control with digital error reset.

The actual mathematical calculations are handled in the digital section of the computer/controller. Salinity, carbon dioxide, pH, oxygen, and hydrogen sulfide would be controlled on a closed-loop basis. Phosphate is added on an open-loop basis at the eductor in the output stream to avoid the possibility of its concentration being reduced by microorganisms during the continuous treatment in the loop. The alkalinity is handled on a combined closed loop/open loop basis because of the physical and chemical interactions operating. The data of Tables 7 through 9 show the equilibrium alkalinity values at various pH, salinity, carbon dioxide, and temperature levels. These data show that in going from 0 deg C to some higher temperature, increased alkalinity is required to maintain equilibrium among fixed values of pH, carbon dioxide, and salinity. Thus if the alkalinity, carbon dioxide, and pH parameters were adjusted to equilibrium in a solution of fixed salinity, temperature, and pressure, and then this solution were warmed to some higher temperature (or subjected to a higher pressure), equilibrium would no longer prevail. Some anticipatory effect is therefore necessary. The slow step, K_0 , indicated in equation (2) prohibits any practical dependence upon a chemical shift to achieve the desired adjustment. The present design provides for the addition of alkalinity at the eductor to make up the deficiency that is created by the change of temperature and pressure. Thus alkalinity control involves closed-loop control in the recirculating stream and open-loop adjustment just before the solution is delivered to the AMF Controlled-Environment System. In effect, then, the chemistry of the output stream is equilibrated with respect to the AMF System environment and must therefore experience that environment quickly to prevent chemical drift. Similarly, in the Sea Water Simulator, accurate control can only be realized if equilibrium conditions are maintained.

In the alkalinity-carbon dioxide-pH system of interacting parameters, only two may be treated as independent parameters at one time. This design establishes pH as always being one of the independent parameters, while the other is to be chosen by the test engineer.

The operation of the simulator will normally involve a one to two hour start-up time. This will include time for filling the loop, and the time required for the output stream to be brought to within the control accuracy. This does not include time for preparation of solutions, standardization, and the like.

B. REAGENTS

The reagents used in the adjustment of composition will include gases and prepared solutions. The gases - nitrogen, oxygen, hydrogen sulfide, and carbon dioxide - will be used neat and not as standardised mixtures. The prepared solutions will include hydrochloric acid (1.0 N), sodium hydroxide (1.0 N), concentrated sea water (70 ppt), sodium bicarbonate solution (500 meq/l alkalinity at 0 deg C), and sodium dihydrogen phosphate solution (30,000 ppm phosphate at 0 deg C). In addition, distilled water will be required.

All the solutions will be made up in distilled water. The hydrochloric acid, sodium hydroxide, and concentrated sea water do not need to be standardised solutions, although the concentrations should be fairly near to the noted values. The alkalinity and phosphate adjusting solutions must be at the pH desired in the output stream and carefully analyzed, as the concentration and density at 0 deg C need to be known accurately. These values are used in the equations utilized by the computer for calculating control points.

C. EXPLANATION OF SYMBOLS

1. System and Concentration Designations

For convenience in discussing the adjustment process and in expressing mathematically the values and relationships of parameters associated with the various steps in the control process, the important sections of the simulator have been assigned number subscripts. The sections are described in the upper left-hand area of Figure 5 (sheet 4) under "Positions or Conditions in the Sea Water Simulator". The solutions for increasing or decreasing concentrations in the sea water stream are also included, giving a total of eight sections numbered 0 through 7. Thus, for example, in a discussion of the system it is convenient to refer to "the flow rate from the loop at $T = 0^{\circ}\text{C}$ and $P = 15$ to 30 psia" simply as $F_{_2}$ or "the density of raw sea water (filtered) as $d_{_5}$.

Similarly the chemical parameters requiring additions, adjustment, or control have been numbered. As indicated in the figure, they have been assigned numbers 1 through 11. Thus "the salinity concentration" is simply C_{01} . The salinity concentration at some specific point may be indicated by adding the section designation. For example, C_{012} represents "the salinity of the adjusted sea water leaving the loop, C_{015} designates the salinity of the raw sea water (filtered), etc." Thus it may be seen that the system, once understood, greatly simplifies the process of referencing certain positions and conditions within the Sea Water Simulator.

A further examination of the situation reveals that the density, volume, weight, and flow rate of sea water at a given point in the system possess one value whether they are being discussed with respect to salinity, to alkalinity, or to any other of the chemical parameters. Thus d_{012} is identical to d_{022} and

F_{023} is identical to F_{033} . For the most part, it is not necessary to maintain the identification between the physical and the chemical parameter. A list of equivalent terms is given in the upper right-hand section of Figure 5 (Sheet 4) together with the equivalent subscript that does not tie it to any specific chemical parameter. This latter, the 00- subscript, is used extensively throughout the drawings and equations. It should be noted, however, that similar relationships do not necessarily apply for the concentrations nor for the volume, weight, density, and flow rate characteristics of solutions added to the sea water stream.

2. Transducer Symbols

The previous section shows the derivation of the terms used in expressing concentrations, volumes, densities, etc. at various points in the sea water simulator. In many cases these parameters will be measured by means of transducers that produce an electrical signal proportional to the quantity expressed by C_{012} , F_{001} , etc. This section explains the symbols used to express these interrelationships.

The transducer symbols employed in the Process Flow Plan, Figure 6 (Sheet 5), follow the Instrument Society of America (ISA) recommended practices. The set point, transducer, indicate and record, and control notations are shown in Figure 4 (Sheet 3). The relationships between the transducer symbols and the quantities they indicate are given in Figure 5 (Sheet 4). The electrical outputs from the transducers are designated simply by X and the quantity being measured. Thus, C_{022} is the alkalinity of the sea water stream coming from the loop at $T = 0^{\circ}\text{C}$ and $P = 15$ to 30 psia, and XC_{022} is the electrical signal produced by the transducer measuring that quantity. Similarly, the reference signals generated by the digital computer are designated by Y and the quantity to be controlled, such as YC_{022} . These relationships are shown in Figure 5 (Sheet 4) and again in Figure 9 (Sheet 8).

VIII.

SUGGESTED CONTROL ACCURACY

The overall control accuracy is based upon the combined errors of the transducers and controllers. The error is minimized in this design by the incorporation of digital error reset. The estimated control accuracy given below is based upon these considerations and upon the assumption of steady-state operation without wide fluctuations in the composition of the incoming sea water. The values listed below compare (1) the tentative values listed in the original statement of work, (2) the transducer accuracies, and (3) the suggested overall control accuracy level.

| <u>Parameter</u> | <u>Control Accuracy</u> | | |
|------------------------------------|-------------------------|-------------------|----------------|
| | <u>Tentative</u> | <u>Transducer</u> | <u>Control</u> |
| Salinity, ppt | 0.01 | 0.03 | 0.035 |
| Alkalinity, meq/l | 0.1 | 0.06 | 0.1 |
| Dissolved free carbon dioxide, ppm | 0.5 | 0.5 | 1.0 |
| pH | 0.02 | 0.02 | 0.03 |
| E_h , mv | 10.0 | 10.0 | * |
| Dissolved oxygen, ml/l | 0.05 | 0.1 | 0.15 |
| Dissolved hydrogen sulfide, ppm | 0.5 | 2.5 | 3.0 |
| Phosphate, ppm | 0.1 | 2.0 | 3.0 |

* The redox potential will not be controlled.

IX. EXPERIMENTAL

Although basically a design effort, this program also included a brief experimental effort. The purpose of this supplementary work was to validate, insofar as practical, the theoretical chemistry implicit in the design and functions of the Sea Water Simulator, and to evaluate the suitability of available commercial sensors for use in such a system. This work is described below.

A. PROCESS VALIDATION TESTS

Chemical manipulations of sea water were performed to demonstrate that the process design recommended here will effect the adjustments predicted, and without introducing unexpected and undesirable results. The experiments selected were intended to reproduce the following key process functions of the Sea Water Simulator: (1) pretreatment, (2) closed-loop adjustment, and (3) final phosphate addition. The aim of step (1) was to demonstrate the efficacy of gas stripping for the reduction of sea water alkalinity (to less than 0.50 meq/l), while the aim of both steps (2) and (3) was to arrive at a product brine having (at 0°C) the following arbitrary composition:

| | |
|---------------------------|---------------------------------|
| Salinity: | 34.00 ppt |
| Alkalinity (carbonate): | 2.24 meq/l (dependent variable) |
| Dissolved carbon dioxide: | 2.00 ppm |
| pH: | 7.80 |
| Dissolved oxygen: | 3.89 ml/l |
| Phosphate: | 25.0 ppm |

A target value of 5.00 ppm of dissolved oxygen was originally planned. Because this fell very close to the analyzed content - 4.95 ppm - of the stock sea water used, the value was changed to that shown. While the above composition was otherwise wholly arbitrary, the choice between using oxygen or hydrogen sulfide was not. The latter gas was found to be absent in the stock (surface) sea water. It was decided, therefore, that test meaning would be enhanced by manipulating the gas (oxygen) of this incompatible pair that would necessarily undergo both the removal and addition processes.

The techniques for reproducing the Sea Water Simulator chemical processes involved the use of conventional laboratory glassware. Because of this, and the difficulty of performing conventional oceanographic analyses on pressurized samples, all of the process effects were accomplished at ambient pressure.

1. Sea Water Analysis

A five-gallon sample of sea water was taken from the Santa Catalina channel at 117°53'W; 33°32'N from a depth of a few feet. This was brought to the laboratory, filtered through an 0.45 μ filter, and analyzed by standard oceanographic techniques. The procedures used were those given by Strickland and Parsons in "A Manual of Sea Water Analyses" (Reference 17).

In the case of alkalinity and dissolved carbon dioxide measurements, supplemental data was obtained, respectively, by acid titrimetry and mass spectrometry. The sulfide analysis was done by the Gustafsson colorimetric method. The following analysis was obtained for this stock sea water.

| <u>Chemical Parameter</u> | <u>Analysis</u> |
|------------------------------------|-----------------|
| 1. Salinity, ppt | 33.75 |
| 2. Alkalinity, meq/l | 2.38 |
| 3. Dissolved carbon dioxide, ppm | 1.0 |
| 4. pH | 7.90 |
| 5. E_h , mv | 143 |
| 6. Dissolved oxygen, ml/l | 4.95 |
| 7. Dissolved hydrogen sulfide, ppm | none detected |
| 8. Phosphate, ppm | 0.024 |

2. Validation of the Pretreatment Process

A 400 ml sample of the filtered, room-temperature sea water was processed to evaluate the efficiency of acid stripping for the removal of carbonate alkalinity. Nitrogen gas, introduced through a fritted glass cylinder, was used to remove the carbon dioxide. Without interrupting the gas flow, the pH of the sea water was carefully lowered to 5.00 with N/10 hydrochloric acid and then, without pausing, returned to the original value (7.90) with N/10 sodium hydroxide. Following this treatment, samples were analyzed and found to contain a residual alkalinity of 0.20 meq/l, which is well below the target value of 0.50 meq/l.

3. Validation of the Closed-loop Adjustment Process

A 3-liter sample of stock sea water was taken through exactly the same pretreatment step as just described. At the completion of the pretreatment, the solution was cooled and maintained at a temperature between 0 and 2°C. Based on Tables 10 and 12, the purge gas was changed from pure nitrogen to a mixture in nitrogen containing 0.071 volume-% CO₂ and 10.1 volume-% O₂ to produce the desired concentrations of dissolved gases in the end product. Following brief equilibration, a measured amount of carbonate alkalinity solution (based on equation 5 and Table 8) and concentrated sea water were added to give the desired product concentrations. The pH was then adjusted to 7.80 using N/10 HCl. The volumes added up to this point were as follows:

| <u>Solution Added</u> | <u>Concentration</u> | <u>Volume, ml</u> |
|------------------------|----------------------|-------------------|
| Untreated sea water | see analysis, above | 3000.0 |
| Hydrochloric acid | 0.100 N | 70.0 |
| Sodium hydroxide | 0.106 N | 13.5 |
| Carbonate alkalinity | 500 meq/l | 14.34 |
| Concentrated sea water | 67.50 ppt | 103.35 |
| Hydrochloric acid | 0.100 N | 7.50 |

4. Phosphate Addition

Phosphate and sodium hydroxide solutions (2.728 and 3.00 ml, respectively) were next added to provide a product brine containing 25.0 ppm phosphate, while maintaining the pH at 7.80.

5. Results

The final product was quickly packaged in zero-ullage containers to prevent the loss of dissolved gases, and was then chemically analyzed. The results obtained are tabulated below together with the target values. Necessarily, certain of the data were based on calculated (asterisked) values derived from volumetric and "by-difference" data. The contribution of phosphate to the total alkalinity, for example, was calculated using equation 12. This is fully consistent with the limitations of the present oceanographic analytical methodology. Replicate values were all within the experimental precision required of the standard oceanographic techniques.

| <u>Chemical Parameter</u> | <u>Goal</u> | <u>Result</u> |
|---------------------------------|-------------|---------------|
| Salinity, ppt | 34.00 | 33.94 |
| pH | 7.80 | 7.80 |
| Alkalinity, meq/l, total | - | 2.84 |
| " " , carbonate | 2.24 | 2.18 * |
| " " , phosphate | - | 0.49 * |
| " " , residual | - | 0.20 |
| Dissolved CO ₂ , ppm | 2.0 | 1.8 |
| E _h , mv | - | 132 |
| Dissolved O ₂ , ml/l | 3.89 | 3.86 |
| Phosphate, ppm | 25.0 | 25.1 |
| Hydrogen sulfide, ppm | 0.0 | 0.0 |

It is obvious from these data that the chemical manipulations implicit in the process design features of the simulator do provide the

expected results. It is also gratifying to note that, with only one small exception, the values obtained fall within the control tolerances suggested in Section VIII. In view of the many manual operations employed in this experiment, results of such quality were not expected.

B. EVALUATION OF COMMERCIAL TRANSDUCERS

Attempts were made to obtain various transducers and measurement systems for laboratory evaluations under conditions approximating those envisioned for the simulator. Efforts to acquire on loan a gas chromatograph for oxygen, carbon dioxide and hydrogen sulfide measurement; an electrolytic titrator for hydrogen sulfide analysis; and a NDIR instrument for carbon dioxide determinations were not met with cooperation. The manufacturer of the carbon dioxide-sensing electrodes, Beckman Instruments, loaned two prototypes for evaluation. The Model 78525 electrode was tested at three carbon dioxide levels - 0, 0.1, and 100 percent using standard electrolyte (1M potassium chloride, 0.01 M in sodium bicarbonate) and electrolyte without the sodium bicarbonate. For both electrolytes the 0 to 100 percent carbon dioxide change gave a deflection of approximately 300 mv, while the 0 to 0.1 percent change produced a deflection of about 3 mv. (The second prototype had essentially the same sensitivity characteristics.) While this latter change is not detectable on a 1400 mv range, the 3 mv signal could be amplified to a measurable deflection by expanding the scale. Unfortunately, this also amplifies the instability and drift of the pH meter used, and at very low carbon dioxide levels this noise could impair the accuracy of readings or mask the change due to carbon dioxide. The response time at low carbon dioxide levels was observed to be on the order of 30 minutes, as stated by the manufacturer. Thus it appears that the sensor would not be applicable for direct determinations of carbon dioxide in sea water at the 0 to 50 ppm level. It might, however, be useful for the determination of carbon dioxide in the gas phase after it had been stripped from the sea water and concentrated by some appropriate method.

X. CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

The technical survey revealed that all the pertinent data with regard to chemical interactions and to physical interaction of salinity and temperature with chemical parameters are available covering the ranges of interest in this system. Data showing the effect of pressure are generally complete up to about 10,000 psi, but data covering the range from 10,000 to 20,000 psi are sparse. This, of course, would not prevent the use of the Sea Water Simulator in the ranges where data are known. Although there is no absolute method of verifying the accuracy of published data, the values used in this design are believed to be the most accurate available at this time. As the information regarding sea water chemistry and interactions are updated, expanded, and improved in accuracy, it would be desirable to incorporate the new values to improve the accuracy of the interaction equations.

The review of commercial transducers shows that devices for the measurement of all eight chemical parameters are available. Many of these commercial analyzers do not provide the full accuracy that was hoped for, and many have a response time that is much longer than is desirable in the analysis and control of a process stream.

The design set forth here involves a combined closed-loop/open-loop control of seven of the eight chemical parameters. The simulator incorporates a digital computer to provide rapid calculation and updating of the control signals, to make digital reset corrections, and to give a continuous reference signal for the controllers without regard to the response times of the transducers. By combining these features, and because the sea water being brought to the simulator for adjustment will have a relatively constant composition, the output stream under steady-state operation can be controlled to an accuracy that is either equal to or only somewhat lower than that originally specified.

B. RECOMMENDATIONS

It is recommended that the study and work completed and the conclusions arrived at under this contract be utilized in planning and executing three further steps in an overall program of determining the chemical properties of sea water.

1. Finalization of Design

The preliminary design provided under this contract should be finalized with a view to the early construction of the Sea Water Simulator. The final design should provide versatility so that results and improved data obtained in its use or derived in later experimentation can be incorporated into its program or control routine.

2. Fabrication

The fabrication of the Sea Water Simulator should be completed as soon as possible so that urgently needed corrosion data can be derived. As an added bonus, the simulator should also find use in the derivation of improved chemical data for sea water and for the evaluation of future transducers.

3. Development of Transducers

It is suggested that more accurate and more rapidly responding transducers be developed, particularly for alkalinity, phosphate, carbon dioxide, and hydrogen sulfide. These improved transducers would greatly benefit the study of the chemical balance in the ocean environment and aid in the understanding of chemical interactions.

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TABLE 1
TYPICAL COMPOSITION OF PACIFIC OCEAN OR
PORT HUENEME SURFACE SEA WATER

| <u>Chemical Parameter</u> | <u>Typical Range</u> |
|---------------------------|----------------------|
| Salinity, ppt | 33.25 to 33.32 * |
| Alkalinity, meq/l | 2.4 to 2.6 |
| Carbon Dioxide, ppm | 16 to 40 |
| pH | 7.62 to 8.17 * |
| E _h , mv | +63 to +187 * |
| Oxygen, ml/l | 5.42 to 5.74 * |
| Hydrogen Sulfide, ppm | 0 |
| Phosphate, ppm | 0.003 to 0.3 |

* Shallow water in the vicinity of USNCEL, Port Hueneme.

TABLE 2

SPECIFIC CONDUCTIVITY OF SEA WATER*

*Conductivity in milliohms/cm

| S, ppt | Temperature, deg C | | | | | |
|-----------|--------------------|--------|--------|--------|--------|--------|
| | 0 | 2 | 10 | 15 | 20 | 25 |
| 31 | 26.005 | 29.968 | 34.131 | 38.467 | 42.954 | 47.584 |
| 32 | 26.771 | 30.843 | 35.122 | 39.579 | 44.192 | 48.951 |
| 33 | 27.535 | 31.716 | 36.110 | 40.688 | 45.426 | 50.314 |
| 34 | 28.298 | 32.588 | 37.096 | 41.794 | 46.656 | 51.671 |
| 35 | 29.060 | 33.457 | 38.080 | 42.896 | 47.882 | 53.025 |
| 36 | 29.820 | 34.325 | 39.061 | 43.996 | 49.105 | 54.374 |

AGC Equations:

$$K = K_0 + a + bT + cT^2 - dT^3$$

$$K_0 = 1.5596$$

$$a = 0.81051S - 0.00070903S^2$$

$$b = 0.084806 + 0.023184S - 0.000032470S^2$$

$$c = -0.0028267 + 0.00030630S - 0.0000024800S^2$$

$$d = -0.000065601 + 0.0000045195S - 0.000000050405S^2$$

$$S = aK - b$$

$$a = 1.31051 - 0.035740T + 0.00067476T^2 - 0.0000065556T^3$$

$$b = 3.0850 + 0.071596T - 0.0021210T^2 + 0.000031778T^3$$

Weyl's Equation:

$$\log K = 0.57627 + 0.892 \log Cl - 0.0001 tc$$

$$t = 25 - T$$

$$c = 88.3 + 0.55t + 0.0107t^2 - Cl(0.145 - 0.002t + 0.0002t^2)$$

TABLE 3
EFFECT OF PRESSURE ON THE ELECTRICAL
CONDUCTANCE OF SEA WATER

| Pressure (decibars above atmospheric pressure) | Temperature, 0.00 deg C | | | Temperature, 5.00 deg C | | | Temperature, 10.00 deg C | | |
|---|-------------------------|--------|--------|-------------------------|--------|-------|--------------------------|--------|-------|
| | 31.00 | S, ppt | | 31.00 | S, ppt | | 31.00 | S, ppt | |
| | | 35.00 | 39.00 | | 35.00 | 39.00 | | 35.00 | 39.00 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1723 | 2.683 | 2.612 | 2.546 | 2.301 | 2.247 | 2.188 | 1.888 | 1.942 | 1.896 |
| 3446 | 5.055 | 4.928 | 4.791 | 4.334 | 4.228 | 4.122 | 3.751 | 2.661 | 3.576 |
| 5169 | 7.127 | 6.940 | 6.761 | 6.120 | 5.968 | 5.818 | 5.305 | 5.174 | 5.052 |
| 6892 | 8.924 | 8.685 | 8.449 | 7.667 | 7.471 | 7.282 | 6.642 | 4.485 | 6.336 |
| 8615 | 10.457 | 10.162 | 9.891 | 8.994 | 8.765 | 8.540 | 7.806 | 7.619 | 7.432 |
| 10338 | 11.739 | 11.410 | 11.094 | 10.170 | 9.861 | 9.593 | 8.791 | 8.571 | 8.364 |

| Pressure (decibars above atmospheric pressure) | Temperature, 15.00 deg C | | | Temperature, 20.00 deg C | | | Temperature, 25.00 deg C | | |
|---|--------------------------|--------|-------|--------------------------|--------|-------|--------------------------|--------|-------|
| | 31.00 | S, ppt | | 31.00 | S, ppt | | 31.00 | S, ppt | |
| | | 35.00 | 39.00 | | 35.00 | 39.00 | | 35.00 | 39.00 |
| 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 1723 | 1.734 | 1.695 | 1.657 | 1.523 | 1.493 | 1.461 | 1.343 | 1.320 | 1.294 |
| 3446 | 3.273 | 3.200 | 3.131 | 2.875 | 2.819 | 2.757 | 2.543 | 2.493 | 2.444 |
| 5169 | 4.632 | 4.528 | 4.426 | 4.072 | 3.985 | 3.901 | 3.596 | 3.525 | 3.459 |
| 6892 | 5.814 | 5.679 | 5.550 | 5.112 | 5.002 | 4.895 | 4.526 | 4.430 | 4.337 |
| 8615 | 6.827 | 6.670 | 6.515 | 6.013 | 5.883 | 5.755 | 5.321 | 5.211 | 5.098 |
| 10338 | 7.692 | 7.512 | 7.330 | 6.782 | 6.631 | 6.476 | 6.002 | 5.881 | 5.748 |

$$\% \text{ Inc.} = (a + b + c + d) \times (1 + e + f)$$

$$\text{where: } a = 1.5192 - 0.045302T + 0.00083089T^2 - 0.000007900T^3$$

$$b = 1.04200 \times 10^{-3}P - 3.3913 \times 10^{-8}P^2 + 3.300 \times 10^{-13}P^3$$

$$c = 4 \times 10^{-4} + 2.577 \times 10^{-5}P - 2.492 \times 10^{-9}P^2$$

$$d = 1.000 - .1535T + .008276T^2 - .0001657T^3$$

$$e = .006950 - .0000766T$$

$$f = 35.00 - S$$

Note: P in this equation has the units, db above atm press. Dividing the coefficients of P by 1.4504 gives P in psig.

TABLE 4
EFFECT OF CHLORINITY AND TEMPERATURE ON pK_{L1}

| <u>Cl, ppt</u> | <u>T, deg C</u> | | | | |
|----------------|-----------------|----------|-----------|-----------|-----------|
| | <u>0</u> | <u>5</u> | <u>10</u> | <u>15</u> | <u>20</u> |
| 16 | 6.18 | 6.14 | 6.11 | 6.07 | 6.05 |
| 17 | 6.17 | 6.13 | 6.10 | 6.06 | 6.04 |
| 18 | 6.16 | 6.12 | 6.09 | 6.06 | 6.03 |
| 19 | 6.15 | 6.11 | 6.08 | 6.05 | 6.02 |
| 20 | 6.14 | 6.10 | 6.07 | 6.05 | 6.01 |
| 21 | 6.13 | 6.09 | 6.06 | 6.03 | 6.00 |

$$pK_{L1} = 6.34 - 0.010 \text{ Cl} - 0.00650T$$

TABLE 5

EFFECT OF CHLORINITY AND TEMPERATURE ON pK_2^1

| <u>Cl, ppt</u> | <u>T, deg C</u> | | | | |
|----------------|-----------------|----------|-----------|-----------|-----------|
| | <u>0</u> | <u>5</u> | <u>10</u> | <u>15</u> | <u>20</u> |
| 16 | 9.46 | 9.40 | 9.35 | 9.29 | 9.23 |
| 17 | 9.44 | 9.38 | 9.32 | 9.27 | 9.21 |
| 18 | 9.42 | 9.36 | 9.30 | 9.25 | 9.19 |
| 19 | 9.40 | 9.34 | 9.28 | 9.23 | 9.17 |
| 20 | 9.38 | 9.32 | 9.26 | 9.21 | 9.15 |
| 21 | 9.36 | 9.30 | 9.25 | 9.19 | 9.13 |

$$pK_2^1 = 9.78 - 0.020 \text{ Cl} - 0.0115T$$

TABLE 6
EFFECT OF PRESSURE ON K_1' AND K_2' OF CARBONIC ACID

| Depth (D), meters | Pressure (P), psig | Increase, % | |
|----------------------|-----------------------|-------------|-------|
| | | K_1 | K_2 |
| 0 | 0 | 0 | 0 |
| 2000 | 2940 | 26 | 9.6 |
| 4000 | 6880 | 58 | 20 |
| 6000 | 8820 | 100 | 32 |
| 10,000 | 14700 | 202 | 55 |

$$\% \text{ Increase in } K_1' = 0.01107D + 0.000000915D^2$$

$$\% \text{ Increase in } K_2' = 0.00470D + 0.0000000300D^2$$

$$D = P/1.470$$

$$pK_{L1}' = -\log \left[4.571 \times 10^{-6} (1.0 + 7.528 \times 10^{-5}P + 4.235 \times 10^{-9}P^2) \right]$$

$$\frac{-0.010 (S-0.030)}{1.805} - 0.0065T$$

$$pK_2' = -\log \left[1.660 \times 10^{-10} (1.0 + 3.196 \times 10^{-5}P + 3.702 \times 10^{-10}P^2) \right]$$

$$\frac{-0.020 (S-0.030)}{1.805} - 0.0115T$$

TABLE 7

EQUILIBRIUM ALKALINITY (meq/l) FOR VARIOUS pH, CARBON DIOXIDE,
AND TEMPERATURE VALUES AT A SALINITY OF 33.0 PPT

| CO ₂ , ppm | pH | | | | | | | | | | | | | | | |
|--------------------------|------|------|------|------|-------|-------|-------|-------|-------|--------|--------|--------|--------|---------|---------|---------|
| | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 | 7.8 | 8.0 | 8.2 | 8.4 | 8.6 | 8.8 | 9.0 |
| T = 0°C | | | | | | | | | | | | | | | | |
| 1 | .016 | .026 | .042 | .066 | .105 | .167 | .266 | .425 | .680 | 1.097 | 1.786 | 2.948 | 4.970 | 8.623 | 15.542 | 29.343 |
| 2 | .033 | .053 | .083 | .132 | .210 | .334 | .532 | .849 | 1.361 | 2.194 | 3.571 | 5.897 | 9.940 | 17.247 | 31.085 | 58.686 |
| 3 | .050 | .079 | .125 | .199 | .315 | .501 | .798 | 1.274 | 2.041 | 3.291 | 5.357 | 8.845 | 14.910 | 25.870 | 46.627 | 88.028 |
| 4 | .066 | .105 | .167 | .265 | .420 | .668 | 1.064 | 1.698 | 2.721 | 4.388 | 7.143 | 11.793 | 19.880 | 34.494 | 62.169 | 117.371 |
| 5 | .083 | .132 | .209 | .331 | .526 | .835 | 1.330 | 2.123 | 3.401 | 5.485 | 8.928 | 14.742 | 24.850 | 43.117 | 77.711 | 146.714 |
| 6 | .100 | .158 | .250 | .397 | .631 | 1.002 | 1.596 | 2.547 | 4.082 | 6.582 | 10.714 | 17.690 | 29.820 | 51.741 | 93.254 | 176.057 |
| 7 | .116 | .184 | .292 | .463 | .736 | 1.170 | 1.862 | 2.972 | 4.762 | 7.679 | 12.500 | 20.639 | 34.790 | 60.364 | 108.796 | 205.399 |
| 8 | .133 | .210 | .334 | .530 | .841 | 1.337 | 2.128 | 3.396 | 5.442 | 8.776 | 14.285 | 23.587 | 39.760 | 68.987 | 124.338 | 234.742 |
| 9 | .149 | .237 | .376 | .596 | .946 | 1.504 | 2.394 | 3.821 | 6.123 | 9.873 | 16.071 | 26.535 | 44.730 | 77.611 | 139.880 | 264.085 |
| T = 10°C | | | | | | | | | | | | | | | | |
| 1 | .019 | .031 | .048 | .077 | .122 | .194 | .309 | .495 | .796 | 1.289 | 2.115 | 3.530 | 6.044 | 10.706 | 19.801 | 38.497 |
| 2 | .038 | .061 | .097 | .154 | .244 | .388 | .619 | .990 | 1.591 | 2.579 | 4.229 | 7.060 | 12.088 | 21.413 | 39.602 | 76.993 |
| 3 | .058 | .092 | .145 | .230 | .366 | .582 | .928 | 1.485 | 2.387 | 3.868 | 6.344 | 10.590 | 18.131 | 32.119 | 59.402 | 115.490 |
| 4 | .077 | .122 | .194 | .307 | .488 | .776 | 1.238 | 1.980 | 3.183 | 5.157 | 8.458 | 14.121 | 24.175 | 42.825 | 79.203 | 153.986 |
| 5 | .096 | .153 | .242 | .384 | .610 | .971 | 1.547 | 2.475 | 3.978 | 6.447 | 10.573 | 17.651 | 30.219 | 53.532 | 99.004 | 192.483 |
| 6 | .115 | .183 | .290 | .461 | .732 | 1.165 | 1.857 | 2.969 | 4.774 | 7.736 | 12.688 | 21.181 | 36.263 | 64.238 | 118.805 | 230.979 |
| 7 | .135 | .214 | .339 | .538 | .854 | 1.359 | 2.166 | 3.464 | 5.570 | 9.025 | 14.802 | 24.711 | 42.307 | 74.945 | 138.605 | 269.476 |
| 8 | .154 | .244 | .387 | .615 | .976 | 1.553 | 2.475 | 3.959 | 6.365 | 10.315 | 16.917 | 28.241 | 48.351 | 85.651 | 158.406 | 307.973 |
| 9 | .173 | .275 | .436 | .691 | 1.098 | 1.747 | 2.785 | 4.454 | 7.161 | 11.604 | 19.032 | 31.771 | 54.394 | 96.357 | 178.207 | 346.469 |
| T = 20°C | | | | | | | | | | | | | | | | |
| 1 | .022 | .035 | .056 | .089 | .142 | .225 | .360 | .577 | .932 | 1.519 | 2.516 | 4.256 | 7.423 | 13.466 | 25.614 | 51.328 |
| 2 | .045 | .071 | .112 | .178 | .283 | .451 | .720 | 1.154 | 1.864 | 3.039 | 5.031 | 8.513 | 14.846 | 26.931 | 51.229 | 102.657 |
| 3 | .067 | .106 | .168 | .267 | .425 | .676 | 1.080 | 1.731 | 2.795 | 4.558 | 7.547 | 12.769 | 22.269 | 40.397 | 76.843 | 153.985 |
| 4 | .089 | .141 | .224 | .356 | .566 | .902 | 1.440 | 2.309 | 3.727 | 6.078 | 10.062 | 17.026 | 29.692 | 53.865 | 102.458 | 205.313 |
| 5 | .111 | .177 | .280 | .445 | .708 | 1.127 | 1.800 | 2.886 | 4.659 | 7.597 | 12.578 | 21.282 | 37.115 | 67.329 | 128.072 | 256.642 |
| 6 | .134 | .212 | .336 | .534 | .849 | 1.352 | 2.159 | 3.463 | 5.591 | 9.117 | 15.093 | 25.538 | 44.538 | 80.794 | 153.686 | 307.970 |
| 7 | .156 | .247 | .392 | .623 | .991 | 1.578 | 2.519 | 4.040 | 6.522 | 10.636 | 17.609 | 29.795 | 51.962 | 94.260 | 179.301 | 359.299 |
| 8 | .178 | .283 | .449 | .712 | 1.132 | 1.803 | 2.879 | 4.617 | 7.454 | 12.156 | 20.124 | 34.051 | 59.385 | 107.726 | 204.915 | 410.627 |
| 9 | .200 | .318 | .505 | .801 | 1.274 | 2.028 | 3.239 | 5.194 | 8.386 | 13.675 | 22.640 | 38.307 | 66.808 | 121.192 | 230.529 | 461.955 |

TABLE 8
EQUILIBRIUM ALKALINITY (meq/l) FOR VARIOUS pH, CARBON DIOXIDE,
AND TEMPERATURE VALUES AT A SALINITY OF 34.9 PPT

| | | pH | | | | | | | | | | | | |
|--------------------------|-------|------|------|------|-------|-------|-------|-------|-------|--------|--------|--------|--------|---------|
| | | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 | 7.8 | 8.0 | 8.2 | 8.4 |
| CO ₂ , ppm | T=0°C | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 | 7.8 | 8.0 | 8.2 | 8.4 |
| | | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 | 7.8 | 8.0 | 8.2 | 8.4 |
| 1 | 0.017 | .027 | .043 | .068 | .107 | .171 | .272 | .433 | .695 | 1.121 | 1.826 | 3.018 | 5.094 | 8.855 |
| 2 | .034 | .054 | .085 | .135 | .215 | .341 | .543 | .867 | 1.390 | 2.242 | 3.652 | 6.035 | 10.188 | 17.709 |
| 3 | .051 | .081 | .128 | .203 | .322 | .512 | .815 | 1.300 | 2.085 | 3.363 | 5.478 | 9.053 | 15.281 | 26.564 |
| 4 | .068 | .107 | .170 | .270 | .429 | .682 | 1.086 | 1.734 | 2.779 | 4.484 | 7.303 | 12.071 | 20.375 | 35.419 |
| 5 | .085 | .134 | .212 | .338 | .537 | .853 | 1.358 | 2.167 | 3.474 | 5.605 | 9.129 | 15.088 | 25.469 | 44.273 |
| 6 | .102 | .161 | .256 | .405 | .644 | 1.023 | 1.629 | 2.601 | 4.169 | 6.725 | 10.955 | 18.106 | 30.563 | 53.128 |
| 7 | .119 | .188 | .298 | .473 | .751 | 1.194 | 1.901 | 3.034 | 4.864 | 7.846 | 12.781 | 21.123 | 35.656 | 61.983 |
| 8 | .135 | .215 | .341 | .541 | .858 | 1.364 | 2.172 | 3.468 | 5.559 | 8.967 | 14.607 | 24.141 | 40.750 | 70.837 |
| 9 | .152 | .242 | .383 | .608 | .966 | 1.535 | 2.444 | 3.901 | 6.254 | 10.088 | 16.433 | 27.159 | 45.844 | 79.692 |
| 1 | .020 | .031 | .049 | .078 | .125 | .198 | .316 | .505 | .813 | 1.318 | 2.163 | 3.615 | 6.199 | 11.004 |
| 2 | .039 | .062 | .099 | .157 | .249 | .396 | .632 | 1.011 | 1.625 | 2.635 | 4.325 | 7.229 | 12.397 | 22.008 |
| 3 | .059 | .093 | .148 | .235 | .374 | .594 | .948 | 1.516 | 2.438 | 3.953 | 6.488 | 10.844 | 18.596 | 33.013 |
| 4 | .079 | .125 | .198 | .314 | .498 | .792 | 1.263 | 2.021 | 3.250 | 5.270 | 8.650 | 14.458 | 24.794 | 44.017 |
| 5 | .098 | .156 | .247 | .392 | .623 | .991 | 1.579 | 2.526 | 4.063 | 6.588 | 10.813 | 18.073 | 30.993 | 55.021 |
| 6 | .118 | .187 | .296 | .470 | .747 | 1.189 | 1.895 | 3.032 | 4.876 | 7.905 | 12.976 | 21.687 | 37.191 | 66.025 |
| 7 | .137 | .213 | .346 | .549 | .872 | 1.387 | 2.211 | 3.537 | 5.688 | 9.223 | 15.136 | 25.302 | 43.390 | 77.029 |
| 8 | .157 | .249 | .395 | .627 | .996 | 1.585 | 2.527 | 4.042 | 6.501 | 10.540 | 17.301 | 28.917 | 49.588 | 88.034 |
| 9 | .177 | .280 | .444 | .705 | 1.121 | 1.783 | 2.843 | 4.547 | 7.313 | 11.858 | 19.464 | 32.531 | 55.787 | 99.038 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124.694 |
| 1 | .023 | .036 | .057 | .091 | .144 | .230 | .367 | .569 | .951 | 1.553 | 2.573 | 4.360 | 7.619 | 13.855 |
| 2 | .045 | .072 | .114 | .182 | .289 | .460 | .734 | 1.178 | 1.903 | 3.105 | 5.146 | 8.720 | 15.238 | 27.710 |
| 3 | .068 | .108 | .172 | .272 | .433 | .690 | 1.102 | 1.767 | 2.854 | 4.658 | 7.719 | 13.081 | 22.857 | 41.565 |
| 4 | .091 | .144 | .229 | .363 | .577 | .920 | 1.469 | 2.356 | 3.806 | 6.211 | 10.293 | 17.441 | 30.476 | 55.419 |
| 5 | .114 | .180 | .286 | .454 | .722 | 1.150 | 1.836 | 2.946 | 4.757 | 7.764 | 12.866 | 21.801 | 38.095 | 69.274 |
| 6 | .136 | .216 | .343 | .545 | .866 | 1.380 | 2.203 | 3.535 | 5.709 | 9.316 | 15.439 | 26.161 | 45.714 | 83.129 |
| 7 | .159 | .252 | .400 | .636 | 1.011 | 1.610 | 2.571 | 4.124 | 6.660 | 10.869 | 18.012 | 30.522 | 53.333 | 96.984 |
| 8 | .182 | .288 | .457 | .726 | 1.155 | 1.839 | 2.938 | 4.713 | 7.612 | 12.422 | 20.585 | 34.882 | 60.952 | 110.839 |
| 9 | .204 | .324 | .515 | .817 | 1.299 | 2.069 | 3.305 | 5.302 | 8.563 | 13.974 | 23.158 | 39.242 | 68.571 | 124 |

TABLE 9

EQUILIBRIUM ALKALINITY (meq/l) FOR VARIOUS pH, CARBON DIOXIDE,
AND TEMPERATURE VALUES AT A SALINITY OF 35.0 PPT

| CO ₂ , ppm | pH | | | | | | | | | | | | | | | |
|--------------------------|--------|------|------|------|-------|-------|-------|-------|-------|--------|--------|--------|--------|---------|---------|---------|
| | 6.0 | 6.2 | 6.4 | 6.6 | 6.8 | 7.0 | 7.2 | 7.4 | 7.6 | 7.8 | 8.0 | 8.2 | 8.4 | 8.6 | 8.8 | 9.0 |
| T=0°C | 1 .017 | .027 | .043 | .069 | .110 | .174 | .277 | .443 | .710 | 1.145 | 1.867 | 3.089 | 5.221 | 9.093 | 16.466 | 31.260 |
| | 2 .035 | .055 | .087 | .138 | .219 | .348 | .554 | .885 | 1.419 | 2.291 | 3.734 | 6.177 | 10.442 | 18.185 | 32.932 | 62.520 |
| | 3 .052 | .082 | .130 | .207 | .329 | .522 | .832 | 1.328 | 2.129 | 3.436 | 5.601 | 9.266 | 15.662 | 27.278 | 49.399 | 93.780 |
| | 4 .069 | .110 | .174 | .276 | .438 | .696 | 1.109 | 1.771 | 2.839 | 4.581 | 7.468 | 12.354 | 20.883 | 36.371 | 65.865 | 125.040 |
| | 5 .086 | .137 | .217 | .345 | .548 | .871 | 1.386 | 2.213 | 3.549 | 5.727 | 9.335 | 15.443 | 26.104 | 45.463 | 82.331 | 156.300 |
| | 6 .104 | .164 | .261 | .414 | .657 | 1.045 | 1.663 | 2.656 | 4.258 | 6.872 | 11.202 | 18.531 | 31.325 | 54.556 | 98.797 | 187.560 |
| | 7 .121 | .192 | .304 | .483 | .767 | 1.219 | 1.941 | 3.098 | 4.968 | 8.018 | 13.068 | 21.620 | 36.546 | 63.648 | 115.263 | 218.820 |
| | 8 .138 | .219 | .348 | .552 | .876 | 1.393 | 2.218 | 3.541 | 5.678 | 9.163 | 14.935 | 24.708 | 41.766 | 72.741 | 131.730 | 250.080 |
| | 9 .156 | .247 | .391 | .621 | .986 | 1.567 | 2.495 | 3.984 | 6.387 | 10.308 | 16.802 | 27.797 | 46.987 | 81.834 | 148.196 | 281.340 |
| T=10°C | 1 .020 | .032 | .050 | .080 | .127 | .202 | .322 | .516 | .830 | 1.346 | 2.212 | 3.701 | 6.358 | 11.311 | 21.030 | 41.123 |
| | 2 .040 | .064 | .101 | .160 | .254 | .404 | .645 | 1.032 | 1.660 | 2.693 | 4.423 | 7.402 | 12.715 | 22.622 | 42.059 | 82.247 |
| | 3 .060 | .095 | .151 | .240 | .381 | .606 | .967 | 1.548 | 2.490 | 4.039 | 6.635 | 11.103 | 19.073 | 33.934 | 63.089 | 123.370 |
| | 4 .080 | .127 | .202 | .320 | .508 | .809 | 1.289 | 2.063 | 3.320 | 5.385 | 8.847 | 14.804 | 25.430 | 45.245 | 84.119 | 164.493 |
| | 5 .100 | .159 | .252 | .400 | .635 | 1.011 | 1.612 | 2.579 | 4.150 | 6.732 | 11.059 | 18.505 | 31.788 | 56.556 | 105.149 | 205.617 |
| | 6 .120 | .191 | .302 | .480 | .762 | 1.213 | 1.934 | 3.095 | 4.979 | 8.078 | 13.270 | 22.207 | 38.145 | 67.867 | 126.178 | 246.740 |
| | 7 .140 | .222 | .353 | .560 | .889 | 1.415 | 2.257 | 3.611 | 5.809 | 9.424 | 15.482 | 25.908 | 44.503 | 79.179 | 147.208 | 287.863 |
| | 8 .160 | .254 | .403 | .640 | 1.017 | 1.617 | 2.579 | 4.127 | 6.639 | 10.771 | 17.694 | 29.609 | 50.860 | 90.490 | 168.238 | 328.987 |
| | 9 .180 | .286 | .453 | .720 | 1.144 | 1.819 | 2.901 | 4.543 | 7.469 | 12.117 | 19.905 | 33.310 | 57.218 | 101.801 | 189.267 | 370.110 |
| T=20°C | 1 .023 | .037 | .058 | .093 | .147 | .235 | .375 | .601 | .972 | 1.587 | 2.632 | 4.467 | 7.821 | 14.257 | 27.272 | 54.970 |
| | 2 .046 | .074 | .117 | .185 | .295 | .469 | .749 | 1.203 | 1.943 | 3.173 | 5.264 | 8.934 | 15.641 | 28.513 | 54.544 | 109.940 |
| | 3 .070 | .110 | .175 | .278 | .442 | .704 | 1.124 | 1.804 | 2.915 | 4.760 | 7.897 | 13.401 | 23.462 | 42.770 | 81.816 | 164.910 |
| | 4 .093 | .147 | .233 | .370 | .589 | .938 | 1.499 | 2.405 | 3.887 | 6.347 | 10.529 | 17.867 | 31.283 | 57.027 | 109.088 | 219.880 |
| | 5 .116 | .184 | .292 | .463 | .736 | 1.173 | 1.874 | 3.007 | 4.858 | 7.933 | 13.161 | 22.334 | 39.103 | 71.283 | 136.359 | 274.850 |
| | 6 .139 | .221 | .350 | .556 | .884 | 1.407 | 2.248 | 3.608 | 5.830 | 9.520 | 15.793 | 26.801 | 46.924 | 85.540 | 163.631 | 329.820 |
| | 7 .162 | .257 | .408 | .648 | 1.031 | 1.642 | 2.623 | 4.209 | 6.801 | 11.107 | 18.425 | 31.268 | 54.745 | 99.797 | 190.903 | 384.791 |
| | 8 .185 | .294 | .467 | .741 | 1.178 | 1.877 | 2.998 | 4.810 | 7.773 | 12.694 | 21.058 | 35.735 | 62.565 | 114.053 | 218.175 | 439.761 |
| | 9 .209 | .331 | .525 | .834 | 1.325 | 2.111 | 3.373 | 5.412 | 8.745 | 14.280 | 23.690 | 40.202 | 70.386 | 128.310 | 245.447 | 494.731 |

TABLE 10
EFFECT OF TEMPERATURE AND CHLORINITY
ON THE SOLUBILITY OF CO₂ IN SEA WATER

α_s , moles/liter/atmosphere $\times 10^{-4}$

| <u>T, deg C</u> | <u>Chlorinity, ppt</u> | | | | | |
|-----------------|------------------------|-----------|-----------|-----------|-----------|-----------|
| | <u>16</u> | <u>17</u> | <u>18</u> | <u>19</u> | <u>20</u> | <u>21</u> |
| 0 | 667 | 660 | 653 | 646 | 640 | 633 |
| 2 | 617 | 611 | 605 | 599 | 593 | 587 |
| 4 | 573 | 567 | 562 | 557 | 551 | 546 |
| 6 | 533 | 528 | 524 | 519 | 514 | 509 |
| 8 | 499 | 495 | 490 | 486 | 482 | 477 |
| 10 | 468 | 464 | 460 | 456 | 452 | 448 |
| 12 | 438 | 434 | 431 | 428 | 424 | 421 |
| 14 | 413 | 410 | 406 | 403 | 400 | 396 |
| 16 | 390 | 387 | 384 | 381 | 377 | 374 |
| 18 | 368 | 365 | 362 | 359 | 356 | 354 |
| 20 | 348 | 346 | 343 | 340 | 337 | 335 |
| 22 | 329 | 327 | 324 | 321 | 319 | 317 |

$$\alpha_s = \left[a - b (Cl - 16) \right] \times 10^{-4}$$

$$a = 666.6 - 26.04T + 0.7072T^2 - 0.01008T^3$$

$$b = 6.80 - 0.4160T + 0.01593T^2 - 0.0002784T^3$$

TABLE 11

REDOX POTENTIALS AS A FUNCTION OF
DEPTH AND OXYGEN AND SULFIDE CONCENTRATIONS

| <u>Depth, meters</u> | <u>Redox Potential, mv</u> | <u>Oxygen, ml/l</u> | <u>Sulfide, ml/l</u> |
|--------------------------|--------------------------------|-------------------------|--------------------------|
| 0 | 395 | 5.60 | - |
| 25 | 408 | 7.06 | - |
| 50 | 404 | 5.35 | - |
| 100 | 340 | 1.08 | - |
| 150 | -26 | 0.25 | 0.02 |
| 200 | -88 | 0.08 | 0.67 |
| 300 | -139 | 0 | 1.74 |
| 500 | -170 | 0 | 3.60 |
| 750 | -152 | 0 | 5.29 |
| 1000 | -144 | 0 | 6.15 |
| 1500 | -129 | 0 | 7.34 |

TABLE 12
SOLUBILITY OF OXYGEN IN SEA WATER

| <u>Temp., deg C</u> | <u>Chlorinity, ppt</u> | | | | | |
|-------------------------|------------------------|-----------|-----------|-----------|-----------|-----------|
| | <u>15</u> | <u>16</u> | <u>17</u> | <u>18</u> | <u>19</u> | <u>20</u> |
| 0 | 8.55 | 8.43 | 8.32 | 8.20 | 8.08 | 7.97 |
| 2 | 8.11 | 8.02 | 7.91 | 7.80 | 7.69 | 7.58 |
| 4 | 7.74 | 7.64 | 7.53 | 7.43 | 7.33 | 7.23 |
| 6 | 7.38 | 7.28 | 7.20 | 7.10 | 7.01 | 6.91 |
| 8 | 7.06 | 6.97 | 6.89 | 6.80 | 6.71 | 6.62 |
| 10 | 6.77 | 6.69 | 6.60 | 6.52 | 6.44 | 6.35 |
| 12 | 6.50 | 6.43 | 6.35 | 6.27 | 6.19 | 6.11 |
| 14 | 6.26 | 6.19 | 6.11 | 6.04 | 5.97 | 5.89 |
| 16 | 6.03 | 5.96 | 5.89 | 5.82 | 5.76 | 5.69 |
| 18 | 5.83 | 5.76 | 5.69 | 5.63 | 5.56 | 5.49 |
| 20 | 5.63 | 5.56 | 5.50 | 5.44 | 5.38 | 5.31 |

$$OX = 10.291 + a - b \cdot Cl$$

$$a = -0.2809T + 0.006009T^2 - 0.00006320T^3$$

$$b = 0.1161 - 0.003922T + 0.00006310T^2$$

OX = oxygen solubility, ml/l at NTP in water equilibrated with dry air
at a total pressure of 760 torr.

TABLE 13

DENSITY OF SEA WATER

| Temp., deg C | Salinity, ppt. | | | | | |
|-----------------|----------------|-----------|-----------|-----------|-----------|-----------|
| | <u>30</u> | <u>32</u> | <u>34</u> | <u>36</u> | <u>38</u> | <u>40</u> |
| 0 | 1.02410 | 1.02571 | 1.02732 | 1.02893 | 1.03055 | 1.03216 |
| 2 | 1.02400 | 1.02560 | 1.02719 | 1.02879 | 1.03040 | 1.03200 |
| 4 | 1.02384 | 1.02543 | 1.02701 | 1.02860 | 1.03019 | 1.03179 |
| 6 | 1.02363 | 1.02521 | 1.02678 | 1.02836 | 1.02994 | 1.03153 |
| 8 | 1.02340 | 1.02494 | 1.02651 | 1.02808 | 1.02965 | 1.03122 |
| 10 | 1.02308 | 1.02464 | 1.02619 | 1.02775 | 1.02931 | 1.03088 |
| 15 | 1.02215 | 1.02364 | 1.02522 | 1.02676 | 1.02830 | 1.02985 |
| 20 | 1.02098 | 1.02250 | 1.02402 | 1.02554 | 1.02707 | 1.02860 |

$$d = a + b(S-30)$$

$$a = 1.02411 - 0.0000472004T - 0.00000549012T^2$$

$$b = 0.000806199 - 0.00000314213T + 0.0000000469203T^2$$

TABLE 14

SPECIFIC VOLUME OF SEA WATER

| Pressure, Bars | Temperature, deg C | | | | |
|-------------------|--------------------|--------|--------|--------|--------|
| | 0 | 5 | 10 | 15 | 20 |
| S = 30.52 ppt | | | | | |
| 1 | 0.9761 | 0.9764 | 0.9771 | 0.9779 | 0.9791 |
| 100 | .9715 | .9720 | .9728 | .9737 | .9749 |
| 200 | .9672 | .9677 | .9686 | .9696 | .9708 |
| 300 | .9629 | .9636 | .9646 | .9656 | .9669 |
| 400 | .9589 | .9596 | .9606 | .9617 | .9630 |
| 500 | .9547 | .9556 | .9567 | .9579 | .9592 |
| 600 | .9508 | .9518 | .9530 | .9542 | .9556 |
| 700 | .9471 | .9481 | .9493 | .9506 | .9521 |
| 800 | .9434 | .9445 | .9458 | .9471 | .9486 |
| 900 | .9398 | .9409 | .9423 | .9437 | .9452 |
| 1000 | .9364 | .9375 | .9389 | .9403 | .9418 |
| 1200 | .9298 | .9311 | .9325 | .9340 | .9356 |
| 1300 | .9267 | .9281 | .9295 | .9311 | .9327 |
| S = 34.99 ppt | | | | | |
| 1 | .9726 | .9730 | .9737 | .9747 | .9758 |
| 100 | .9682 | .9687 | .9695 | .9705 | .9717 |
| 200 | .9639 | .9645 | .9654 | .9664 | .9677 |
| 300 | .9598 | .9605 | .9614 | .9625 | .9638 |
| 400 | .9557 | .9566 | .9575 | .9587 | .9600 |
| 500 | .9518 | .9527 | .9537 | .9549 | .9563 |
| 600 | .9480 | .9489 | .9500 | .9513 | .9527 |
| 700 | .9443 | .9453 | .9465 | .9478 | .9492 |
| 800 | .9406 | .9417 | .9430 | .9444 | .9458 |
| 900 | .9371 | .9383 | .9396 | .9410 | .9424 |
| 1000 | .9337 | .9349 | .9363 | .9377 | .9392 |
| 1100 | .9303 | .9316 | .9330 | .9344 | .9360 |
| 1200 | .9271 | .9284 | .9298 | .9313 | .9329 |
| 1300 | .9240 | .9253 | .9268 | .9283 | .9299 |
| S = 41.03 ppt | | | | | |
| 1 | .9680 | .9685 | .9693 | .9703 | .9714 |
| 100 | .9637 | .9643 | .9652 | .9662 | .9674 |
| 200 | .9595 | .9602 | .9611 | .9622 | .9635 |
| 300 | .9554 | .9562 | .9572 | .9583 | .9597 |
| 400 | .9514 | .9523 | .9534 | .9545 | .9559 |
| 500 | .9476 | .9485 | .9497 | .9509 | .9523 |
| 600 | .9438 | .9448 | .9460 | .9473 | .9487 |
| 700 | .9402 | .9413 | .9425 | .9438 | .9453 |
| 800 | .9366 | .9378 | .9390 | .9404 | .9419 |
| 900 | .9332 | .9344 | .9357 | .9371 | .9386 |
| 1000 | .9298 | .9311 | .9324 | .9338 | .9353 |
| 1100 | .9265 | .9278 | .9292 | .9307 | .9322 |
| 1200 | .9233 | .9247 | .9261 | .9276 | .9292 |
| 1300 | .9202 | .9216 | .9231 | .9246 | .9262 |

TABLE 14 (cont'd)

$$1/\text{density} = a - bP + cP^2$$

$$\text{where: } a = d + eT + fT^2$$

$$b = (g - hT + iT^2) \times 10^{-4}$$

$$c = (j - kT + lT^2) \times 10^{-8}$$

$$d = (0.97612 - 0.0007900m + 0.1563 \times 10^{-5}m^2)$$

$$e = (0.4408 + 0.02906m + 0.001407m^2) \times 10^{-4}$$

$$f = (0.5286 - 0.0008978m - 0.0009502m^2) \times 10^{-5}$$

$$g = (0.45824 - 0.004632m + 0.0002114m^2)$$

$$h = (0.3088 - 0.02354m + 0.001131m^2) \times 10^{-2}$$

$$i = (0.6397 - 0.05537m + 0.001547m^2) \times 10^{-4}$$

$$j = (0.60133 - 0.02428m + 0.001429m^2)$$

$$k = (1.081 - 0.1644m + 0.008846m^2) \times 10^{-2}$$

$$l = (0.2890 - 0.04708m + 0.001888m^2) \times 10^{-3}$$

$$m = (S - 30.52)$$

$$1 \text{ bar} = 14.504 \text{ psi}$$

FORTRAN IV PROGRAM FOR CARBONATE ALKALINITY

```

C SFA WATER STIMULATOR H C EDGINGTON
C A=PK1-R=PK2-C=CO2.D=DENSITY.P=PH.S=SALINITY.T=TEMPERATURE
C T=1.3(T) J=1.3(S) K=1.9(C) L=1.16(P)
      DIMENSION C(9).P(16).S(3).T(3)
      NAMELIST/X/C.P.S.T
      NAMELIST/Y/K.L.J.A.R.D.ALKY
      10 READ(5,X)
      DO 50 J=1.3
      DO 50 I=1.3
      DO 50 L=1.16
      DO 50 K=1.9
      D=1.02411-4.72*10.**(-5)*T(I)-5.4901*10.** -6)*T(I)**2.+
      1(8.062*10.**(-3)-3.1421*10.**(-5)*T(I)-4.692*10.**(-7)*T(I)**2.)*
      1 (S(J)-30.0)
      A=6.34-0.010*(S(J)-0.030)/1.805-0.0065*T(I)
      R=9.78-0.020*(S(J)-0.030)/1.805-0.0115*T(I)
      ALKY=0.02722*(K)*D*10.**P(L)*(1.+2.*10.**P(L)/10.**A
      WRITE(6,Y)
      50 CONTINUE
      GO TO 10
      END

```

Figure 1

INDEX

| SHEET | TITLE |
|-------|----------------------------------|
| 1 | INDEX |
| 2 | EQUIPMENT LIST |
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| 5 | PROCESS FLOW PLAN |
| 6 | FUNCTIONAL BLOCK DIAGRAM OF T |
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| 8 | COMPUTER CORRECTIONS |
| 9 | COMPUTER CORRECTIONS |
| 10 | BLOCK DIAGRAMS OF THE ANALOG |
| 11 | BLOCK DIAGRAMS OF THE ANALOG |
| 12 | BLOCK DIAGRAMS OF THE ANALOG |

ON
EFFECTIVE
USAGI

A

DEX

TITLE

DEX

EQUIPMENT LIST

INSTRUMENTATION CODE

IDENTIFICATION OF PHYSICAL AND CHEMICAL PARAMETERS

PROCESS FLOW PLAN

FUNCTIONAL BLOCK DIAGRAM OF THE COMPUTER/CONTROLLER

FUNCTIONAL DETAILS OF THE DIGITAL COMPUTER

COMPUTER CORRECTIONS

COMPUTER CORRECTIONS

BLOCK DIAGRAMS OF THE ANALOG CONTROLLERS

BLOCK DIAGRAMS OF THE ANALOG CONTROLLERS

BLOCK DIAGRAMS OF THE ANALOG CONTROLLERS

| SYN | | CODE IDENT | PART OR IDENTIFYING NO. | NOMENCLATURE OR DESCRIPTION | MATERIAL | SPECIFICATION | UNIT WT | ZONE | ITEM NO |
|---|--|------------|-------------------------|--|----------|---|---------|------|---------|
| LIST OF MATERIALS | | | | | | | | | |
| UNLESS OTHERWISE SPECIFIED DIMENSIONS ARE IN INCHES TOLERANCES ON DECIMALS X1 = .03 X2 = .010 DO NOT SCALE DRAWING | | | | DRAWN BY: S. TYBURN CHECKED BY: J. J. J. DATE: 7-19-66 TITLE: SEA WATER SIMULATOR AEROJET-GENERAL CORPORATION AZUSA, CALIFORNIA | | | | | |
| EFFECTIVE SERIAL NO. USAGE DATA | | | | APPLICATION | | DRAWING NO. 093562 | | | |
| DRAWING LEVEL | | | | O | | SCALE: NONE RELEASE DATE: 7/27 SHEET 1 OF 2 | | | |

093562

Figure 2

EQUIPMENT LIST

T-1 TANK, ALKALINITY PREADJUSTMENT, WITH MIXER
 T-2 TANK, pH ADJUSTMENT, WITH MIXER
 T-3 TANK, PHOSPHATE, FEED
 T-4 TANK, ALKALINITY, FEED
 T-5 TANK, DISTILLED WATER, FEED
 T-6 TANK, CONCENTRATED SEA WATER, FEED
 T-7 TANK, SODIUM HYDROXIDE, FEED
 T-8 TANK, HYDROCHLORIC ACID, FEED
 T-9 TANK, NITROGEN HUMIDIFIER
 T-10 TANK, PHOSPHATE, MAKE-UP, WITH MIXER (NOT SHOWN)
 T-11 TANK, ALKALINITY, MAKE-UP, WITH MIXER (NOT SHOWN)
 T-12 TANK, CONCENTRATED SEA WATER, MAKE-UP, WITH MIXER (NOT SHOWN)
 T-13 TANK, SODIUM HYDROXIDE, MAKE-UP, WITH MIXER (NOT SHOWN)
 T-14 TANK, HYDROCHLORIC ACID, MAKE-UP, WITH MIXER (NOT SHOWN)
 T-15 TANK, STANDARD SOLUTIONS FOR CALIBRATION, WITH MIXER AND SIGHT GLASS

P-1 PUMP, INCOMING SEA WATER
 P-2 PUMP, FILTERED AND PRETREATED SEA WATER
 P-3 PUMP, METERING, PHOSPHATE ADDITION
 P-4 PUMP, METERING, ALKALINITY DIFFERENTIAL ADDITION
 P-5 PUMP, METERING, ALKALINITY ADDITION
 P-6 PUMP, METERING, DISTILLED WATER ADDITION
 P-7 PUMP, METERING, CONCENTRATED SEA WATER ADDITION
 P-8 PUMP, METERING, NaOH FOR pH PRETREATMENT
 P-9 PUMP, METERING, SODIUM HYDROXIDE ADDITION
 P-10 PUMP, METERING, HCL FOR ALKALINITY PRETREATMENT
 P-11 PUMP, METERING, HYDROCHLORIC ACID ADDITION
 P-12 PUMP, MIXING COLUMN RECIRCULATION
 P-13 PUMP, STANDARD SOLUTION RECIRCULATION

M-1 MIXING COLUMN

F-1 PREFILTERS (2)
 F-2 FILTERS (2)

J-1 EDUCTOR, PHOSPHATE AND ALKALINITY ADDITION

E-1 PRECOOLER, INCOMING SEA WATER
 E-2 COOLER, RECIRCULATING LOOP, TOP
 E-3 COOLER, RECIRCULATING LOOP, BOTTOM
 E-4 COOLER, STANDARD SOLUTION
 E-5 HEAT EXCHANGER, ADJUSTMENT TO TEMPERATURE OF AMF TEST SYSTEM

R-1 REFRIGERATION SYSTEM

CV-1 CONTROL VALVE, AUTOMATIC, FLOW TO T-1
 CV-2 CONTROL VALVE, AUTOMATIC, FLOW TO M-1
 CV-3 CONTROL VALVE, AUTOMATIC, FLOW FROM R-1
 CV-4 CONTROL VALVE, AUTOMATIC, FLOW TO ADJUSTED STREAM
 CV-5 CONTROL VALVE, AUTOMATIC, N₂ FLOW TO M-1
 CV-6 CONTROL VALVE, AUTOMATIC, O₂ CONTROL
 CV-7 CONTROL VALVE, AUTOMATIC, CO₂ CONTROL
 CV-8 CONTROL VALVE, AUTOMATIC, H₂S CONTROL

A

COMPONENT LIST

INSTRUMENTATION COLUMN

TEMPERATURES (2)
PRESSURES (2)

FOR, PHOSPHATE AND ALKALINITY
ANALYSIS

COOLER, INCOMING SEA WATER
HEATER, RECIRCULATING LOOP, TOP
HEATER, RECIRCULATING LOOP, BOTTOM
HEATER, STANDARD SOLUTION
HEAT EXCHANGER, ADJUSTMENT TO
TEMPERATURE OF AMF TEST SYSTEM

VALVE REGULATION SYSTEM

CONTROL VALVE, AUTOMATIC,
FLOW TO T-1
CONTROL VALVE, AUTOMATIC,
FLOW TO M-1
CONTROL VALVE, AUTOMATIC,
FLOW FROM R-1
CONTROL VALVE, AUTOMATIC,
FLOW TO ADJUSTED STREAM
CONTROL VALVE, AUTOMATIC,
FLOW TO M-1
CONTROL VALVE, AUTOMATIC,
CONTROL
CONTROL VALVE, AUTOMATIC,
CONTROL
CONTROL VALVE, AUTOMATIC,
CONTROL

- V-1 VALVE, MANUAL, TWO-WAY, FILTER
STREAM SELECTOR
- V-2 VALVE, MANUAL, TWO-WAY, FILTER
STREAM SELECTOR
- V-3 VALVE, MANUAL, TWO-WAY, FILTER
STREAM SELECTOR
- V-4 VALVE, MANUAL, TWO-WAY, FILTER
STREAM SELECTOR
- V-5 VALVE, MANUAL, FOUR-WAY, ANALYZER-
CALIBRATION STREAM SELECTOR
- V-6 VALVE, MANUAL, FOUR-WAY, ANALYZER-
CALIBRATION STREAM SELECTOR
- V-7 VALVE, MANUAL, FLOW ADJUSTMENT IN
RECIRCULATING LOOP
- V-8 VALVE, MANUAL, THREE-WAY, PURGE GAS
CONTROL FOR T-1
- V-9 VALVE, MANUAL, PURGE GAS TO ANALYZER
SECTION
- V-10 VALVE, MANUAL, SHUTOFF AT T-3
- V-11 VALVE, MANUAL, SHUTOFF AT T-4
- V-12 VALVE, MANUAL, SHUTOFF AT T-5
- V-13 VALVE, MANUAL, SHUTOFF AT T-6
- V-14 VALVE, MANUAL, SHUTOFF AT T-7
- V-15 VALVE, MANUAL, SHUTOFF AT T-8
- V-16 VALVE, MANUAL, SHUTOFF AT P-1
- V-17 VALVE, MANUAL, SHUTOFF AT P-2
- V-18 VALVE, MANUAL, SHUTOFF AT P-12
- V-19 VALVE, MANUAL, THROTTLING AT P-13

INSTRUMENTATION CODE
(ISA NOMENCLATURE & SYMBOLS)

| | SET POINT | TRANSducer | INDICATE |
|---|-----------|------------|----------|
| 1. ANALYSIS AND CONTROL PARAMETERS | | | |
| A. SALINITY | AS 1 | AT 1 | AR 1 |
| B. ALKALINITY | AS 2 | AT 2 | AR 2 |
| C. DISSOLVED FREE CARBON DIOXIDE | AS 3 | AT 3 | AR 3 |
| D. pH | AS 4 | AT 4 | AR 4 |
| E. E _H | AS 5 | AT 5 | AR 5 |
| F. DISSOLVED OXYGEN | AS 6 | AT 6 | AR 6 |
| G. DISSOLVED HYDROGEN SULFIDE | AS 7 | AT 7 | AR 7 |
| H. PHOSPHATE | AS 8 | AT 8 | AR 8 |
| I. ALKALINITY, DIFFERENTIAL | AS 9 | AT 9 | AR 9 |
| J. ALKALINITY, PRE ADJUSTMENT | AS 10 | AT 10 | AR 10 |
| K. pH PREADJUSTMENT | AS 11 | AT 11 | AR 11 |
| L. ALKALINITY, CHECK | AS 12 | AT 12 | AR 12 |
| 2. LEVEL | | | |
| A. INCOMING, TANK 1, ALKALINITY REMOVAL | LT 1 | LT 1 | AR 1 |
| B. EQUILIBRATOR TANK, MIXER M-1 | LT 2 | LT 2 | AR 2 |
| 3. PRESSURE | | | |
| A. INCOMING SEA WATER | PT 1 | PT 1 | AR 1 |
| B. FLOW LOOP, AT EXIT | PT 2 | PT 2 | AR 2 |
| C. AT USE, IN AMF TEST DEVICE | PT 3 | PT 3 | AR 3 |
| 4. TEMPERATURE | | | |
| A. FLOW LOOP, TOP | TT 1 | TT 1 | AR 1 |
| B. FLOW LOOP AT EXIT | TT 2 | TT 2 | AR 2 |
| C. REFRIGERATION SYSTEM R-1 | TT 3 | TT 3 | AR 3 |
| D. AT USE, IN AMF TEST DEVICE | TT 4 | TT 4 | AR 4 |
| E. CALIBRATION STREAM | TT 5 | TT 5 | AR 5 |
| 5. FLOW | | | |
| A. INCOMING SEA WATER STREAM, 1 GPM | FT 1 | FT 1 | AR 1 |
| B. NITROGEN GAS | FT 2 | FT 2 | AR 2 |
| C. LOOP, 20 GPM | FT 3 | FT 3 | AR 3 |
| D. ADJUSTED STREAM, 1 GPM AT 0°C | FT 4 | FT 4 | AR 4 |
| E. PHOSPHATE ADDITION | FT 5 | FT 5 | AR 5 |
| F. ALKALINITY DIFFERENTIAL | FT 6 | FT 6 | AR 6 |
| G. CALIBRATION STREAM | FT 7 | FT 7 | AR 7 |
| 6. DENSITY | | | |
| A. ADJUSTED STREAM | DT 1 | DT 1 | AR 1 |

UMENTATION CODE
 MENCLATURE + SYMBOLS, RP 5.1)

SIGNAL

| JCER | INDICATE, RECORD, ALARM | RECORD, CONTROL |
|-------|----------------------------|--------------------|
| AT 2 | AIR 1 | AC 1a,b |
| AT 4 | AIR 2 | AC 2 |
| AT 5 | AIR 3 | AC 3 |
| AT 6 | AIR 4 | AC 4a |
| AT 7 | AIR 5 | AC 6 |
| AT 8 | AIR 6 | AC 7 |
| AT 9 | AIR 7 | AC 8 |
| AT 10 | AIR 8 | AC 9 |
| AT 11 | — | AC 10 |
| AT 12 | — | AC 11 |
| AT 13 | — | — |
| AT 14 | — | LC 1 |
| AT 15 | — | LC 2 |
| AT 16 | PIA 1 | — |
| AT 17 | PIA 2 | — |
| AT 18 | — | — |
| AT 19 | TI 1 | — |
| AT 20 | TI 2 | — |
| AT 21 | TI 3 | TRC 3 |
| AT 22 | TI 4 | — |
| AT 23 | TI 5 | — |
| AT 24 | FI 1 | — |
| AT 25 | FI 2 | FRC 2 |
| AT 26 | FI 3 | — |
| AT 27 | FI 4 | FRC 4 |
| AT 28 | — | AC 8 |
| AT 29 | — | AC 9 |
| AT 30 | FI 7 | — |
| AT 31 | — | — |

099562

70143 099562

Figure 4

IDENTIFICATION OF PHYSICAL AND CHEMICAL PARAMETERS

| POSITIONS OR CONDITIONS IN THE SEA WATER SIMULATOR | 0. VALUES EQUIV. FOR ALL CHEMICAL PARAMETERS | 1. SALINITY, PT. (WT) | 2. ALKALINITY, mg/L | 3. CO ₂ , ppm (WT) | 4. pH | 5. Eh | 6. O ₂ , ml/L | 7. H ₂ S, ppm (WT) | 8. PHOSPHATE, ppm (WT) | 9. ALKALINITY DIFFERENTIAL, mg/L | 10. ALKALINITY PREADJUSTMENT, mg/L | 11. pH PREALJUSTMENT |
|---|--|-----------------------|---------------------|-------------------------------|-------|-------|--------------------------|-------------------------------|------------------------|----------------------------------|------------------------------------|----------------------|
| 0. FINAL, AT USE T: 0° TO 20°C P: 0 TO 20,000 PSIA | 000 | 010 | 020 | 030 | 040 | 050 | 060 | 070 | 080 | | | |
| 1. FINAL T: 0°C P: 15 TO 30 PSIA | 001 | 011 | 021 | 031 | 041 | 051 | 061 | 071 | 081 | | | |
| 2. FROM LOOP T: 0°C P: 15 TO 30 PSIA | 002 | 012 | 022 | 032 | 042 | 052 | 062 | 072 | 082 | | | |
| 3. WITHIN LOOP AFTER INCOMING SEA WATER BEFORE REAGENT ADDITION T: 0°C P: 15 TO 30 PSIA | 003 | 013 | 023 | 033 | 043 | 053 | 063 | 073 | 083 | | | |
| 4. ENTERING LOOP (PREADJUSTED) T: 0°C P: 15 TO 30 PSIA | 004 | 014 | 024 | 034 | 044 | 054 | 064 | 074 | 084 | | | |
| 5. RAW SEA WATER (FILTERED) | 005 | 015 | 025 | 035 | 045 | 055 | 065 | 075 | 085 | | | |
| 6. MAKE-UP FOR INCREASING CONC | | 016 | 026 | 036 | 046 | | 066 | 076 | 086 T: 0°C | 096 T: 0°C | | 116 |
| 7. MAKE-UP FOR DECREASING CONC | | 017 | | 037 | 047 | | 067 | 077 | | | 107 | |

NOTES:

1. THE NUMBERS WITHIN EACH BLOCK ARE SUBSCRIPTS REFERENCING SOLUTION PARAMETERS AT SPECIFIC POINTS IN THE SEA WATER SIMULATOR.

2. THE SOLUTION PARAMETERS TO BE SUBSCRIPTED AS INDICATED IN NOTE 1 ARE:

C, CONCENTRATION (OR VALUE)

V, VOLUME, ml

W, WEIGHT, g

d, DENSITY, g/ml

F, FLOW RATE, ml/min

THUS: C₀₂ REPRESENTS THE SALINITY OF THE SEA WATER LEAVING THE LOOP.

3. A VACANT BOX INDICATES THAT NO SUCH CONDITION, SOLUTION, OR MEASUREMENT IS MADE OR REQUIRED IN THE SEA WATER SIMULATOR.

| 3. DIFFERENTIAL mV/L | 0. ALKALINITY PREADJUST- MENT, mV/L | 11. pH PREADJUSTMENT |
|-------------------------|---|-------------------------|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| 96 °C | | 116 |
| | 107 | |

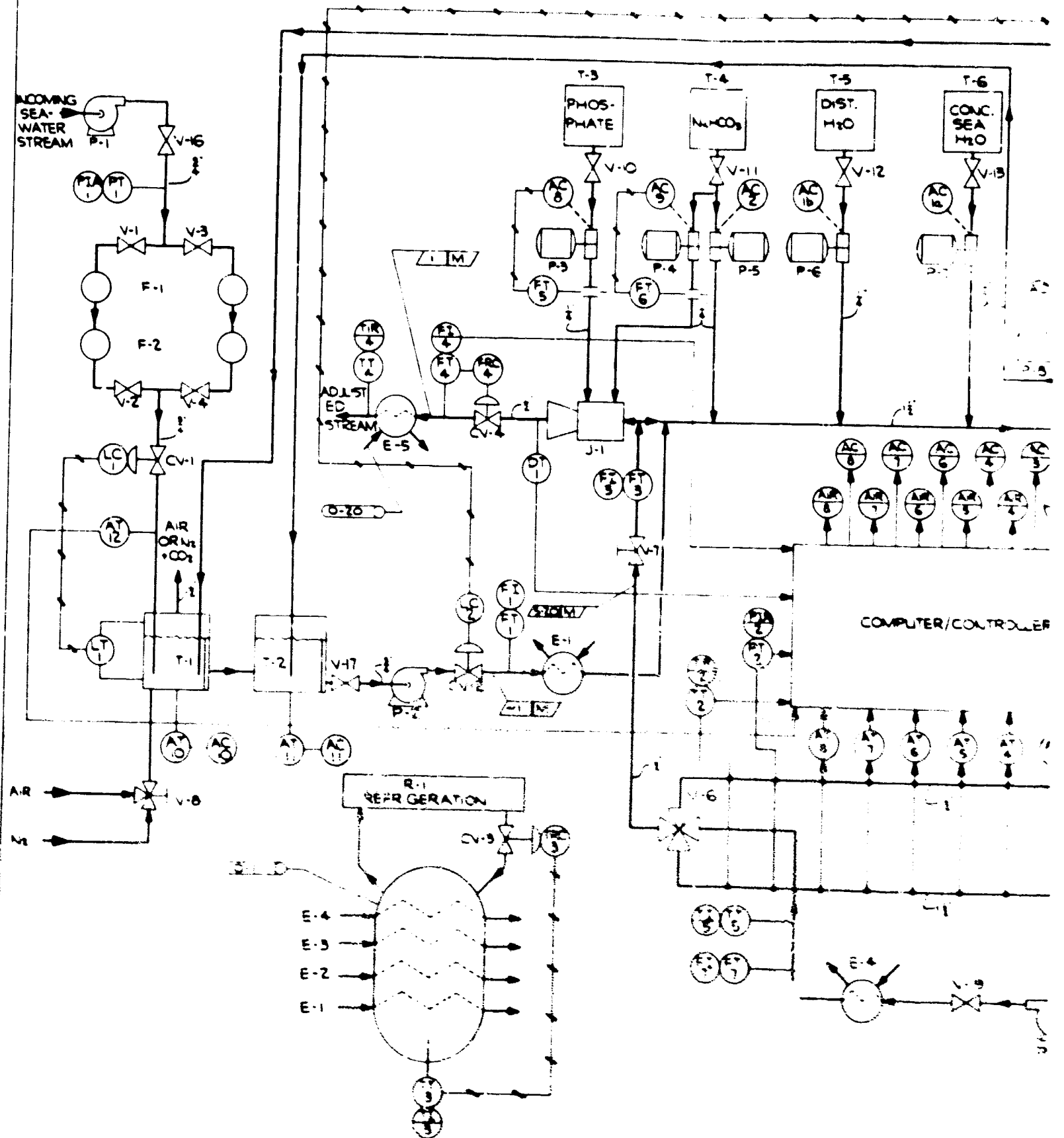
LIST OF EQUIVALENT TERMS

- $V_{000} : V_{010} : V_{020} : V_{030} : V_{040} : V_{050} : V_{060} : V_{070} : V_{080}$
 $W_{000} : W_{010} : W_{020} : W_{030} : W_{040} : W_{050} : W_{060} : W_{070} : W_{080}$
 $d_{000} : d_{010} : d_{020} : d_{030} : d_{040} : d_{050} : d_{060} : d_{070} : d_{080}$
 $F_{000} : F_{010} : F_{020} : F_{030} : F_{040} : F_{050} : F_{060} : F_{070} : F_{080}$
- $V_{001} : V_{011} : V_{021} : V_{031} : V_{041} : V_{051} : V_{061} : V_{071} : V_{081}$
 $W_{001} : W_{011} : W_{021} : W_{031} : W_{041} : W_{051} : W_{061} : W_{071} : W_{081}$
 $d_{001} : d_{011} : d_{021} : d_{031} : d_{041} : d_{051} : d_{061} : d_{071} : d_{081}$
 $F_{001} : F_{011} : F_{021} : F_{031} : F_{041} : F_{051} : F_{061} : F_{071} : F_{081}$
- $V_{002} : V_{012} : V_{022} : V_{032} : V_{042} : V_{052} : V_{062} : V_{072} : V_{082}$
 $W_{002} : W_{012} : W_{022} : W_{032} : W_{042} : W_{052} : W_{062} : W_{072} : W_{082}$
 $d_{002} : d_{012} : d_{022} : d_{032} : d_{042} : d_{052} : d_{062} : d_{072} : d_{082}$
 $F_{002} : F_{012} : F_{022} : F_{032} : F_{042} : F_{052} : F_{062} : F_{072} : F_{082}$
- $V_{003} : V_{013} : V_{023} : V_{033} : V_{043} : V_{053} : V_{063} : V_{073} : V_{083}$
 $W_{003} : W_{013} : W_{023} : W_{033} : W_{043} : W_{053} : W_{063} : W_{073} : W_{083}$
 $d_{003} : d_{013} : d_{023} : d_{033} : d_{043} : d_{053} : d_{063} : d_{073} : d_{083}$
 $F_{003} : F_{013} : F_{023} : F_{033} : F_{043} : F_{053} : F_{063} : F_{073} : F_{083}$
- $V_{004} : V_{014} : V_{024} : V_{034} : V_{044} : V_{054} : V_{064} : V_{074} : V_{084}$
 $W_{004} : W_{014} : W_{024} : W_{034} : W_{044} : W_{054} : W_{064} : W_{074} : W_{084}$
 $d_{004} : d_{014} : d_{024} : d_{034} : d_{044} : d_{054} : d_{064} : d_{074} : d_{084}$
 $F_{004} : F_{014} : F_{024} : F_{034} : F_{044} : F_{054} : F_{064} : F_{074} : F_{084}$
- $V_{005} : V_{015} : V_{025} : V_{035} : V_{045} : V_{055} : V_{065} : V_{075} : V_{085}$
 $W_{005} : W_{015} : W_{025} : W_{035} : W_{045} : W_{055} : W_{065} : W_{075} : W_{085}$
 $d_{005} : d_{015} : d_{025} : d_{035} : d_{045} : d_{055} : d_{065} : d_{075} : d_{085}$
 $F_{005} : F_{015} : F_{025} : F_{035} : F_{045} : F_{055} : F_{065} : F_{075} : F_{085}$

| TRANSDUCER SYMBOL | INPUT VALUE | ELECTRICAL INPUT | CONTROL SIGNAL OUTPUT |
|--|----------------|---------------------|--------------------------|
| $\text{PT} \begin{smallmatrix} 1 \\ 2 \end{smallmatrix}$ | P002 | XP002 | |
| $\text{T} \begin{smallmatrix} 1 \\ 2 \end{smallmatrix}$ | T002 | XT002 | |
| $\text{DO} \begin{smallmatrix} 1 \\ 1 \end{smallmatrix}$ | D001 | XD001 | |
| $\text{CO} \begin{smallmatrix} 1 \\ 1 \end{smallmatrix}$ | C011 | XC011 | YK012 |
| $\text{CO} \begin{smallmatrix} 2 \\ 1 \end{smallmatrix}$ | C021 | XC021 | YC012, YF014 |
| $\text{CO} \begin{smallmatrix} 3 \\ 1 \end{smallmatrix}$ | C031 | XC031 | YC012 |
| $\text{CO} \begin{smallmatrix} 4 \\ 1 \end{smallmatrix}$ | C041 | XC041 | YC012 |
| $\text{CO} \begin{smallmatrix} 5 \\ 1 \end{smallmatrix}$ | C051 | XC051 | |
| $\text{CO} \begin{smallmatrix} 6 \\ 1 \end{smallmatrix}$ | C061 | XC061 | YC061 |
| $\text{CO} \begin{smallmatrix} 7 \\ 1 \end{smallmatrix}$ | C071 | XC071 | YC071 |
| $\text{CO} \begin{smallmatrix} 8 \\ 1 \end{smallmatrix}$ | C081 | XC081 | YF086 |
| $\text{CO} \begin{smallmatrix} 9 \\ 1 \end{smallmatrix}$ | C091 | XC091 | |
| $\text{FO} \begin{smallmatrix} 1 \\ 1 \end{smallmatrix}$ | F001 | XF001 | |
| $\text{TO} \begin{smallmatrix} 1 \\ 1 \end{smallmatrix}$ | T000 | XT000 | |

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PROCESS FLOW PLAN



| REVENUE | | | | |
|---------|------|-------------|------|-------|
| NO. | DATE | DESCRIPTION | AMT. | TOTAL |
| | | | | |

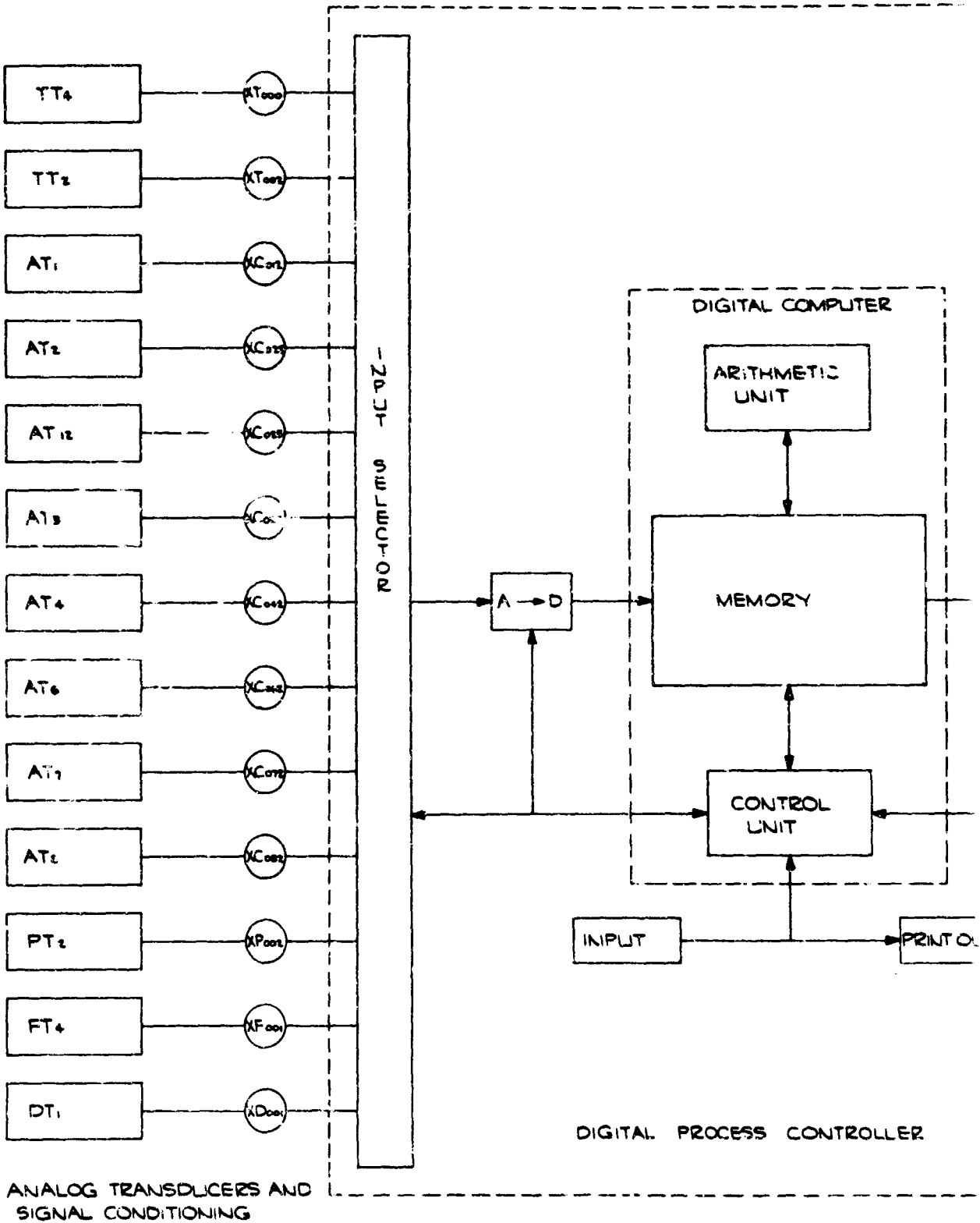


○ · TEMPERATURE, °C

1

Figure 6

FUNCTIONAL BLOCK DIAGRAM OF THE COMPUTER

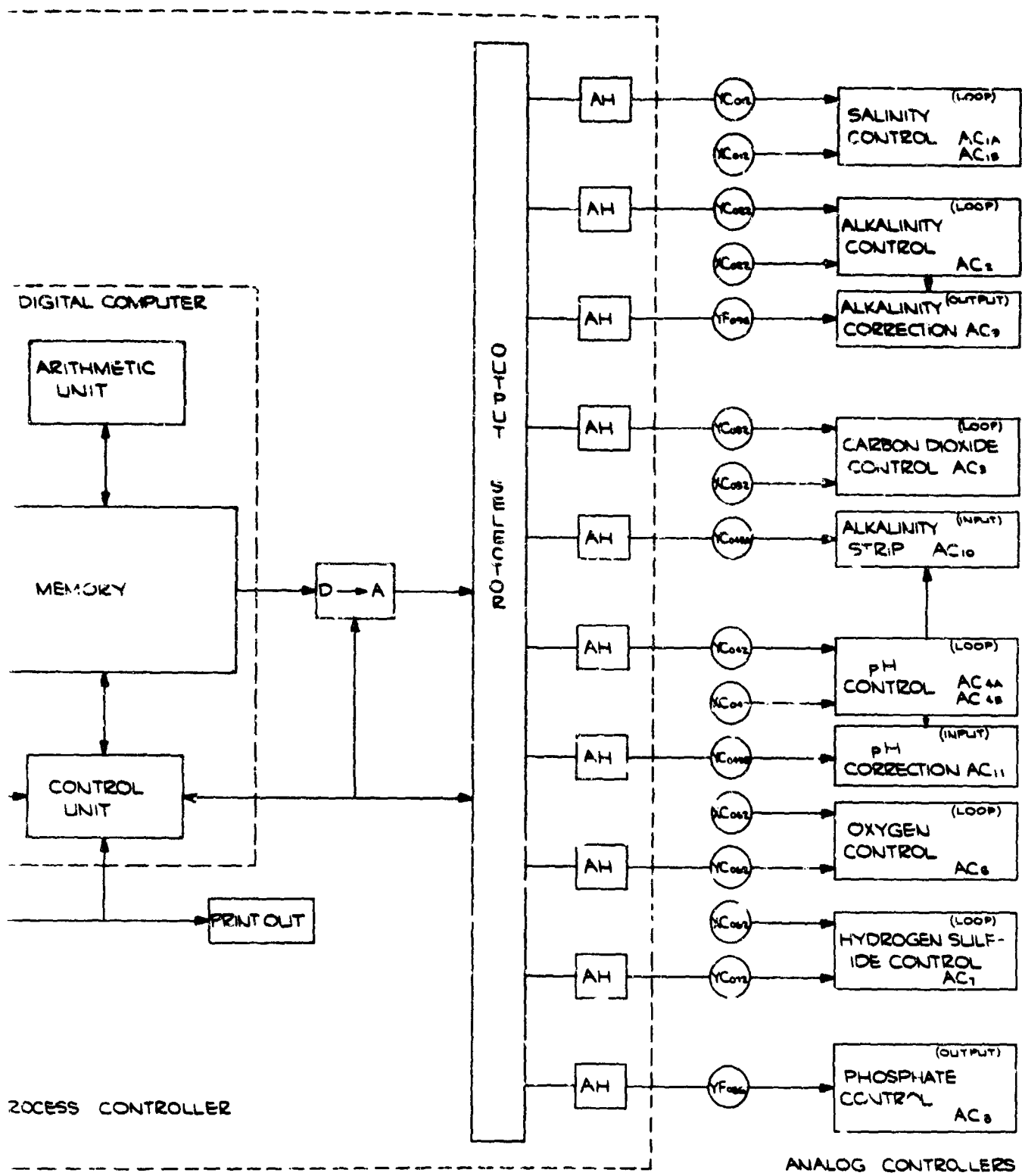


NOTES:

1. $A \rightarrow D$ = ANALOG TO DIGITAL CONVERSION.
2. $D \rightarrow A$ = DIGITAL TO ANALOG CONVERSION.
3. A.H = ANALOG HOLD CIRCUIT.

A

DIAGRAM OF THE COMPUTER/CONTROLLER

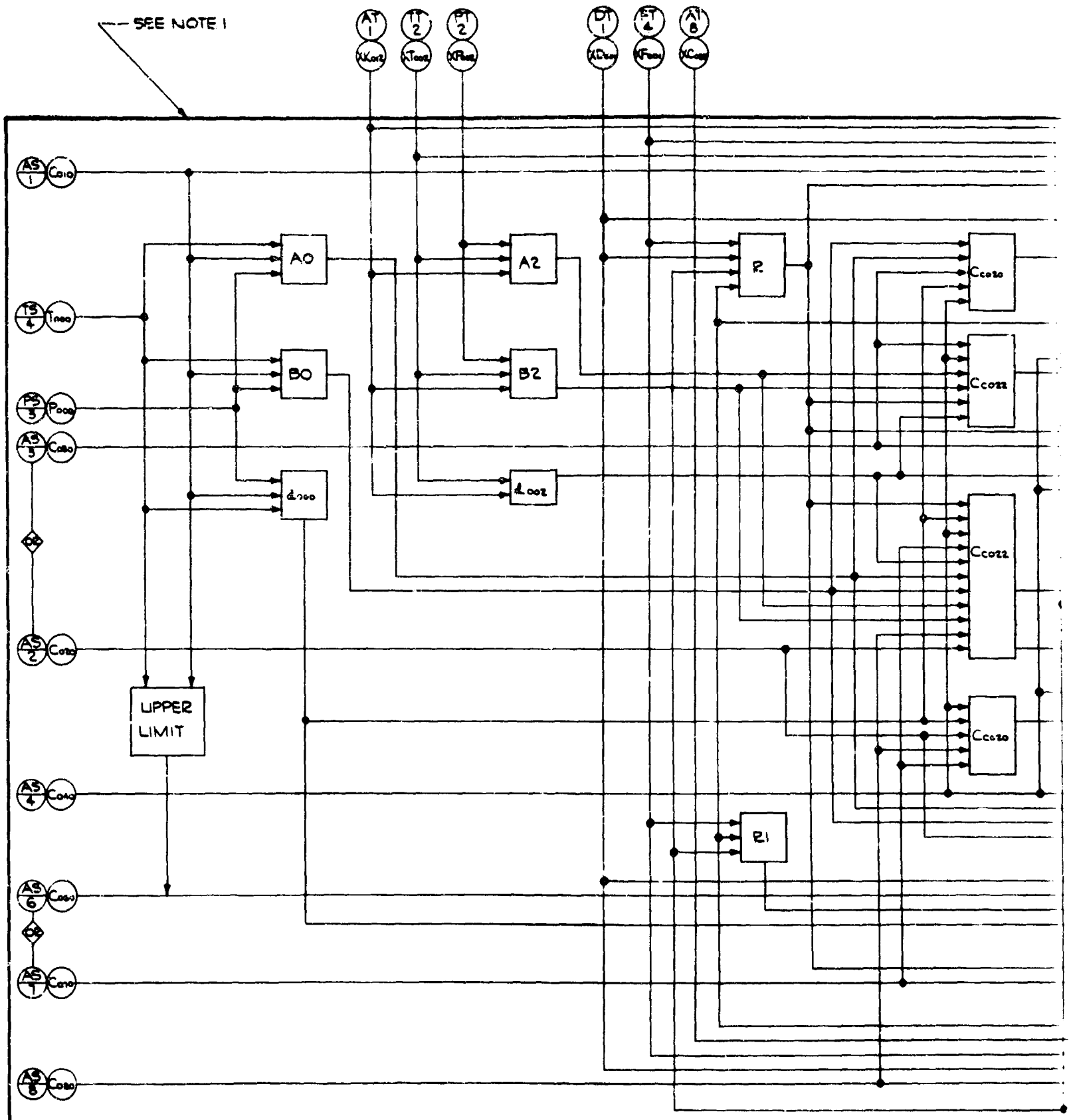


TO DIGITAL CONVERSION.
 TO ANALOG CONVERSION.
 OLD CIRCUIT.

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 2-7-67 6

Figure 7

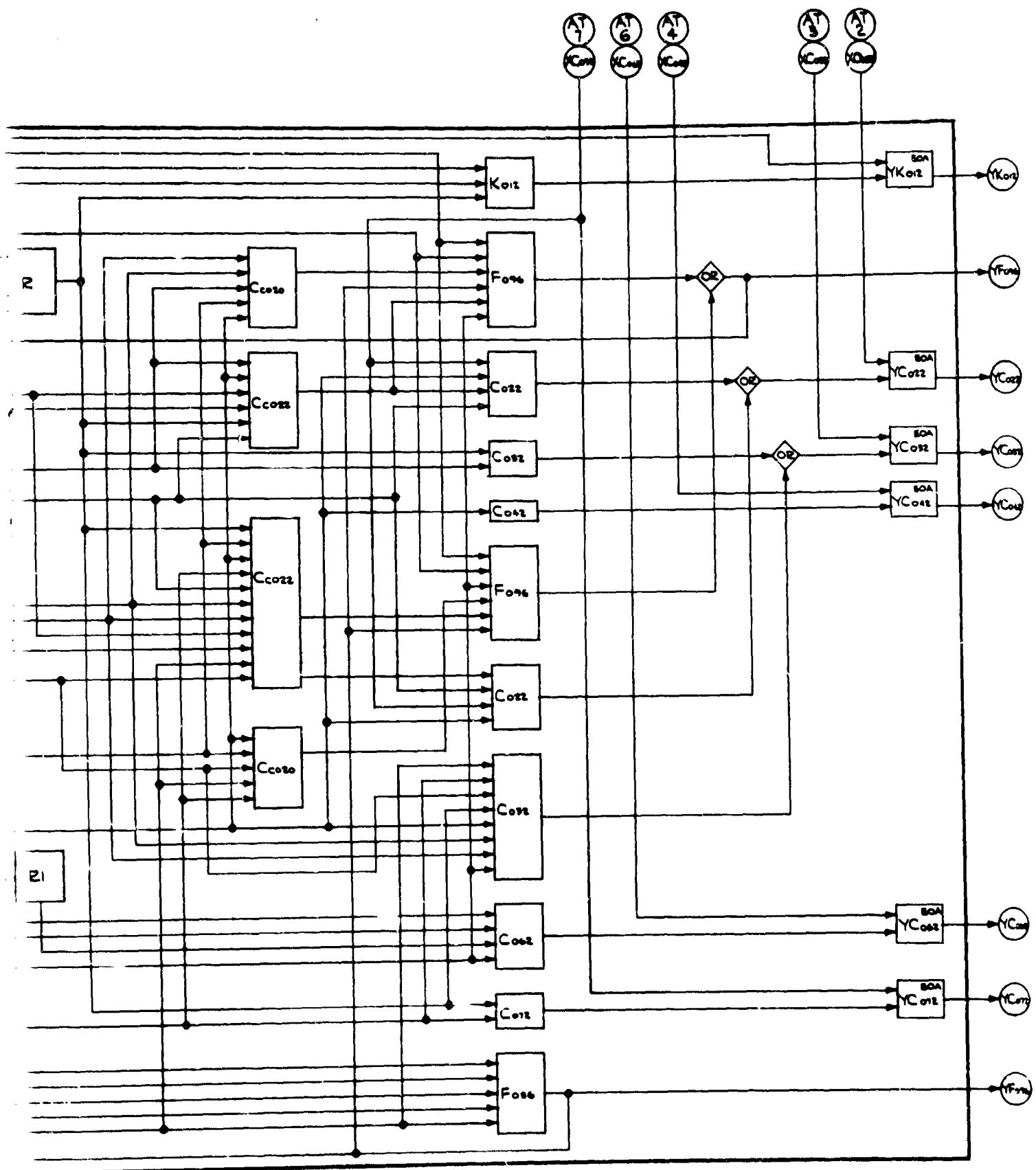
FUNCTIONAL DETAILS OF THE DIGITAL COMPUTER



NOTES:

1. CROSSING TO THE INSIDE OF THIS AREA INVOLVES ANALOG TO DIGITAL (A TO D) CONVERSION, WHILE THE REVERSE INVOLVES D TO A CONVERSION.

2. THE NUMBERS WITHIN THE INDIVIDUAL BOXES IN THE DIGITAL SECTION REFER TO SIGNAL CORRECTIONS INDICATED ON SHEETS 8 & 9.



THE INDIVIDUAL BOXES IN
REFER TO SIGNAL
ED ON SHEETS 8 & 9.

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Figure 8

CALCULATED FACTORS

$$R = \frac{d_{001} F_{001}}{d_{001} F_{001} - d_{002} F_{002} - d_{003} F_{003}}$$

$$R1 = \frac{F_{001}}{F_{001} - F_{002} - F_{003}}$$

$$d_{000} = \frac{1}{(a \cdot b P_{000} + c (P_{000})^2)}$$

$$a = (d + e T_{000} + f (T_{000})^2)$$

$$b = (g - h T_{000} + i (T_{000})^2) \times 10^{-4}$$

$$c = (j - k T_{000} + l (T_{000})^2) \times 10^{-8}$$

$$d = (0.97612 - 0.1900 \times 10^{-3} m + 0.1563 \times 10^{-5} m^2)$$

$$e = (0.4408 + 0.02906 m + 0.001407 m^2) \times 10^{-4}$$

$$f = (0.5286 - 0.8978 \times 10^{-3} m - 0.9502 \times 10^{-5} m^2) \times 10^{-8}$$

$$g = (0.45824 - 0.004632 m + 0.0002114 m^2)$$

$$h = (0.3088 - 0.02354 m + 0.001131 m^2) \times 10^{-2}$$

$$i = (0.6397 - 0.05537 m + 0.001547 m^2) \times 10^{-4}$$

$$j = (0.60133 - 0.02428 m + 0.001429 m^2)$$

$$k = (1.081 - 0.1644 m - 0.008846 m^2) \times 10^{-2}$$

$$l = (0.2890 - 0.04708 m + 0.001888 m^2) \times 10^{-3}$$

$$m = (C_{010} - 30.52)$$

$$d_{002} = n + \sigma (C_{012} - 30)$$

$$n = 1.02411 - 4.7200 \times 10^{-5} (T_{002}) - 5.4901 \times 10^{-6} (T_{002})^2$$

$$\sigma = 8.0620 \times 10^{-5} - 3.1421 \times 10^{-5} (T_{002}) - 4.6920 \times 10^{-7} (T_{002})^2$$

$$C_{012} = PK_{012} - q$$

$$p = 1.31051 - 3.5740 \times 10^{-2} (T_{002}) + 6.7476 \times 10^{-4} (T_{002})^2 - 6.5556 \times 10^{-6} (T_{002})^3$$

$$q = 3.0850 + 7.1596 \times 10^{-2} (T_{002}) - 2.1210 \times 10^{-3} (T_{002})^2 + 3.1778 \times 10^{-5} (T_{002})^3$$

$$A0 = -\log [4.571 \times 10^{-6} (1.0 + 7.528 \times 10^{-5} (P_{000}) + 4.235 \times 10^{-9} (P_{000})^2)] - \frac{0.010 (C_{010} - 0.030)}{1.805} - 0.0065 (T_{000})$$

$$B0 = -\log [1.660 \times 10^{-10} (1.0 + 3.196 \times 10^{-5} (P_{000}) + 3.702 \times 10^{-10} (P_{000})^2)] - \frac{0.020 (C_{010} - 0.030)}{1.805} - 0.0115 (T_{000})$$

$$A2 = -\log [4.571 \times 10^{-6} (1.0 + 7.528 \times 10^{-5} (P_{002}) + 4.235 \times 10^{-9} (P_{002})^2)] - \frac{0.010 (C_{012} - 0.030)}{1.805} - 0.0065 (T_{002})$$

$$B2 = -\log [1.660 \times 10^{-10} (1.0 + 3.196 \times 10^{-5} (P_{002}) + 3.702 \times 10^{-10} (P_{002})^2)] - \frac{0.020 (C_{012} - 0.030)}{1.805} - 0.0115 (T_{002})$$

UNITS USED IN COMPUTER CORRECTIONS

| PARAMETER | UNIT |
|---|-------------|
| PRESSURE (P_{000}, P_{002}) | psig |
| TEMPERATURE (T_{000}, T_{002}) | °C |
| DENSITY ($d_{000}, d_{001}, d_{002}$) | g/ml |
| FLOW RATE ($F_{001}, F_{002}, F_{003}$) | ml/min |
| SALINITY (C_{010}, C_{012}) | ppt |
| CONDUCTIVITY (K_{012}) | milliohm/cm |
| ALKALINITY ($C_{020}, C_{022}, C_{024}, C_{026}$) | meq/l |
| CARBON DIOXIDE (C_{030}, C_{032}) | ppm |
| pH ($C_{040}, C_{041}, C_{042}$) | - |
| E_u (C_{050}, C_{052}) | mV |
| OXYGEN (C_{060}, C_{062}) | ml/l |
| HYDROGEN SULFIDE (C_{070}, C_{072}) | ppm |
| PHOSPHATE ($C_{080}, C_{082}, C_{084}$) | ppm |

COMPUTER CORRECTIONS

| REVISED | | DESCRIPTION | | DATE | APPROVED |
|---------|--|-------------|--|------|----------|
| | | | | | |

EQUIVALENCE BETWEEN THE INSTRUMENTATION CODE AND MEASURED PARAMETERS AT SET POINTS

$$C_{010} = \left(\frac{AS}{1} \right)$$

$$C_{012} = \left(\frac{AT}{1} \right) = XK_{012}$$

$$C_{020} = \left(\frac{AS}{2} \right) *$$

$$C_{022} = \left(\frac{AT}{2} \right) = XC_{022}$$

$$C_{030} = \left(\frac{AS}{3} \right) *$$

$$C_{032} = \left(\frac{AT}{3} \right) = XC_{032}$$

$$C_{040} = \left(\frac{AS}{4} \right)$$

$$C_{042} = \left(\frac{AT}{4} \right) = XC_{042}$$

$$C_{060} = \left(\frac{AS}{6} \right) *$$

$$C_{062} = \left(\frac{AT}{5} \right)$$

$$C_{070} = \left(\frac{AS}{7} \right) *$$

$$C_{062} = \left(\frac{AT}{6} \right) = XC_{062}$$

$$C_{080} = \left(\frac{AS}{8} \right)$$

$$C_{072} = \left(\frac{AT}{7} \right) = XC_{072}$$

$$P_{000} = \left(\frac{PS}{3} \right)$$

$$C_{082} = \left(\frac{AT}{8} \right) = XC_{082}$$

$$T_{000} = \left(\frac{TS}{4} \right)$$

$$P_{002} = \left(\frac{PT}{2} \right) = XP_{002}$$

$$F_{001} = \left(\frac{FT}{4} \right)$$

$$T_{002} = \left(\frac{TT}{2} \right) = XT_{002}$$

$$d_{001} = \left(\frac{DT}{1} \right) = XD_{001}$$

$$\frac{0.030}{5} - 0.0065(T_{000})$$

$$\frac{0.030}{5} - 0.0115(T_{000})$$

$$\frac{0.030}{305} - 0.0065(T_{002})$$

$$\frac{0.030}{305} - 0.0115(T_{002})$$

* THIS IS TRUE ONLY WHEN THESE QUANTITIES ARE INDEPENDENT VARIABLES.

099562

| | | |
|-------|---|--------|
| 70143 | F | 099562 |
|-------|---|--------|

Figure 9

COMPLTER CORRECTIONS

1. SALINITY BY CONDUCTIVITY:

$$K_{012} = 1.5596 + \tau + s(T_{012}) + t(T_{012})^2 + \mu(T_{012})^3$$

$$\tau = 0.81051(C_{010} \cdot R) - 7.0903 \times 10^{-4}(C_{010} \cdot R)^2$$

$$s = 0.084806 + 0.023184(C_{010} \cdot R) - 3.2470 \times 10^{-5}(C_{010} \cdot R)^2$$

$$t = -0.0028267 + 3.0630 \times 10^{-5}(C_{010} \cdot R) - 2.4800 \times 10^{-6}(C_{010} \cdot R)^2$$

$$\mu = 6.5601 \times 10^{-8} - 4.5195 \times 10^{-8}(C_{010} \cdot R) + 5.0405 \times 10^{-9}(C_{010} \cdot R)^2$$

$$* YK_{012} = 2K_{012} - XK_{012}$$

2,3,4 ALKALINITY, CARBON DIOXIDE AND pH:

NOTE: pH WILL ALWAYS BE AN INDEPENDENT VARIABLE, SO THAT: $C_{040} = C_{041} = C_{042}$

a. ALKALINITY AS THE DEPENDENT VARIABLE, CARBON DIOXIDE AS THE INDEPENDENT VARIABLE:

$$C_{042} = C_{040}$$

$$* YC_{042} = 2C_{042} - XC_{042}$$

$$C_{092} = C_{030} \cdot R$$

$$* YC_{092} = 2C_{092} - XC_{092}$$

$$C_{022} = C_{022} + 0.10 + \frac{C_{022} \cdot d_{002}}{34} \left(\frac{10^{-7.041}}{10^{-(C_{040})} + 10^{-7.041}} \right)$$

$$* YC_{022} = 2C_{022} - XC_{022}$$

$$F_{096} = \frac{(C_{020} \cdot d_{001}/d_{000} - C_{022}) \cdot F_{001} + C_{022} \cdot F_{006}}{(C_{020} - C_{022})}$$

$$* YF_{096} = F_{096}$$

$$C_{010} = 0.022722 \cdot C_{020} \cdot d_{000} \cdot \frac{10^{(C_{040})}}{10^{40}} \left[1.0 + \frac{2 \cdot 10^{(C_{040})}}{10^{80}} \right]$$

$$C_{022} = 0.022722 \cdot C_{020} \cdot d_{002} \cdot R \cdot \frac{10^{(C_{040})}}{10^{42}} \left[1.0 + \frac{2 \cdot 10^{(C_{040})}}{10^{82}} \right]$$

b. CARBON DIOXIDE AS THE DEPENDENT VARIABLE, ALKALINITY AS THE INDEPENDENT VARIABLE.

$$C_{042} = C_{040}$$

$$* YC_{042} = 2C_{042} - XC_{042}$$

$$C_{092} = \frac{\left[C_{020} - \frac{C_{020} \cdot d_{000}}{95} \left(1.0 + \frac{10^{-7.125}}{10^{-(C_{040})} + 10^{-7.125}} \right) - \frac{C_{020} \cdot d_{000}}{34} \left(\frac{10^{-7.041}}{10^{-(C_{040})} + 10^{-7.041}} \right) - 0.10 \right] \cdot R}{0.022722 \cdot d_{000} \cdot \frac{10^{(C_{040})}}{10^{40}} \left[1.0 + \frac{2 \cdot 10^{(C_{040})}}{10^{80}} \right]}$$

$$* YC_{092} = 2C_{092} - XC_{092}$$

$$C_{022} = C_{022} + 0.1$$

$$* YC_{022} = 2C_{022} - XC_{022}$$

$$F_{096} = \frac{(C_{020} \cdot \frac{d_{001}}{d_{000}} - C_{022}) \cdot F_{001} + C_{022} \cdot F_{006}}{(C_{020} - C_{022})}$$

$$* YF_{096} = F_{096}$$

$$C_{010} = C_{020} - \frac{C_{020} \cdot d_{000}}{95} \left(1.0 + \frac{10^{-7.125}}{10^{-(C_{040})} + 10^{-7.125}} \right) - \frac{C_{020} \cdot d_{000}}{34} \left(\frac{10^{-7.041}}{10^{-(C_{040})} + 10^{-7.041}} \right) - 0.10$$

$$C_{022} = \frac{\left[C_{020} - \frac{C_{020} \cdot d_{000}}{95} \left(1.0 + \frac{10^{-7.125}}{10^{-(C_{040})} + 10^{-7.125}} \right) - \frac{C_{020} \cdot d_{000}}{34} \left(\frac{10^{-7.041}}{10^{-(C_{040})} + 10^{-7.041}} \right) - 0.10 \right] \cdot R \cdot d_{002} \cdot 10}{d_{000} \cdot 10^{42} \left[1.0 + \frac{2 \cdot 10^{(C_{040})}}{10^{82}} \right]}$$

NOTES:

1. THE ASTERISK (*)
CONTROL EQUA
PARAMETER.

| REVISION | | DATE | | APPROVED | |
|----------|----|------|----|----------|----|
| REV | NO | REV | NO | REV | NO |
| | | | | | |

COMPUTER CORRECTIONS

5. E_H : E_H WILL BE MEASURED, BUT NOT CONTROLLED

6. OXYGEN:

$$C_{O2} = C_{O2} \cdot R1 \cdot \frac{d_{O2}}{d_{O2}}$$

$$Y_{C_{O2}} = 2C_{O2} - XC_{O2}$$

$$\text{UPPER LIMIT: } C_{O2} = 10.291 - r - w(C_{O2})$$

$$r = 0.2809(T_{O2}) - 0.006009(T_{O2})^2 + 0.00006320(T_{O2})^3$$

$$w = 0.1161 - 0.005922(T_{O2}) + 0.00006310(T_{O2})^2$$

EITHER OXYGEN OR HYDROGEN SULFIDE WILL BE AN INDEPENDENT VARIABLE. THE TWO WILL NOT BE ADDED SIMULTANEOUSLY.

7. HYDROGEN SULFIDE:

$$C_{H2S} = C_{H2S} \cdot R$$

$$Y_{C_{H2S}} = 2C_{H2S} - XC_{H2S}$$

EITHER HYDROGEN SULFIDE OR OXYGEN WILL BE AN INDEPENDENT VARIABLE. THE TWO WILL NOT BE ADDED SIMULTANEOUSLY.

8. PHOSPHATE:

$$F_{O2} = \frac{(C_{O2} - C_{O2}) \cdot d_{O2} \cdot F_{O2} + C_{O2} \cdot d_{O2} \cdot F_{O2}}{(C_{O2} - C_{O2}) \cdot d_{O2}}$$

$$Y_{F_{O2}} = F_{O2}$$

$$\frac{10^{-1.041}}{10^{-1.041} + 10^{-1.041}} - 0.10 \cdot R$$

$$\frac{10^{-1.041}}{10^{-1.041} + 10^{-1.041}} - 0.10 \cdot R \cdot d_{O2} \cdot 10^{10} \left[1.0 + \frac{2 \cdot 10(C_{O2})}{10^{10}} \right]$$

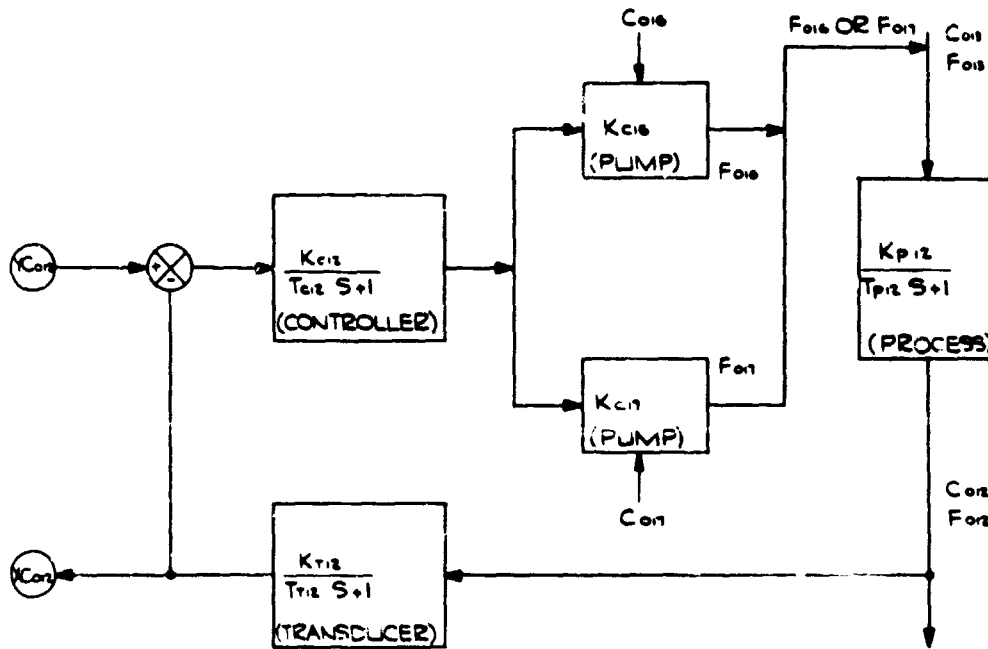
NOTES:

1. THE ASTERISK (*) DENOTES THE FINAL CONTROL EQUATIONS AND THE 10¹⁰ PARAMETER.

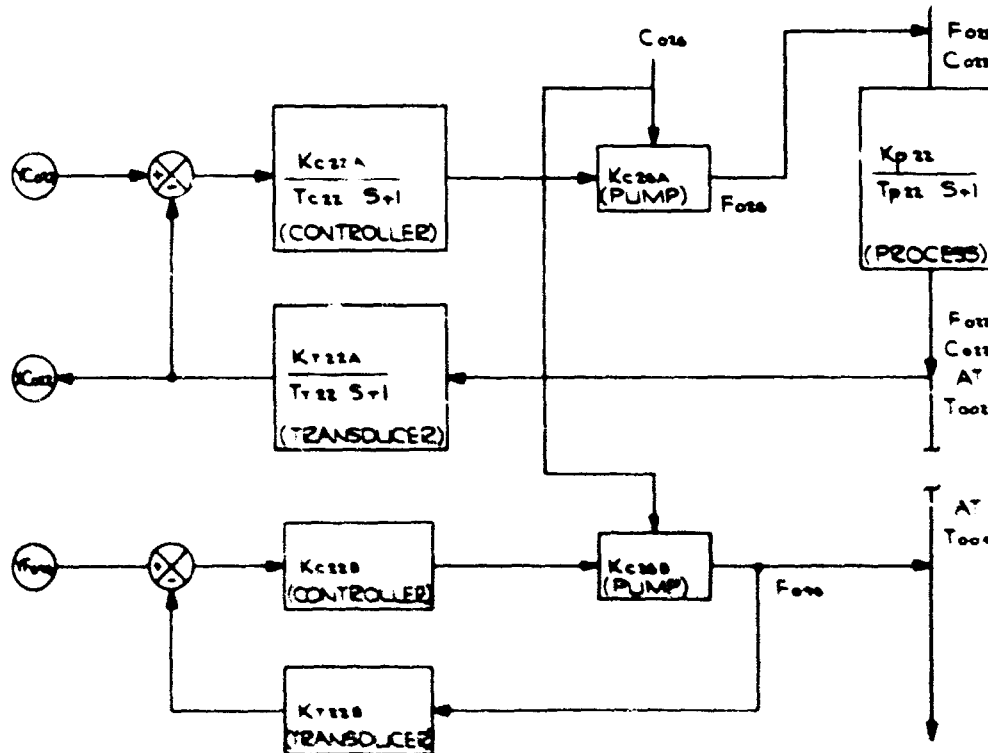
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Figure 10

BLOCK DIAGRAMS OF THE ANALOG CONTROLLER



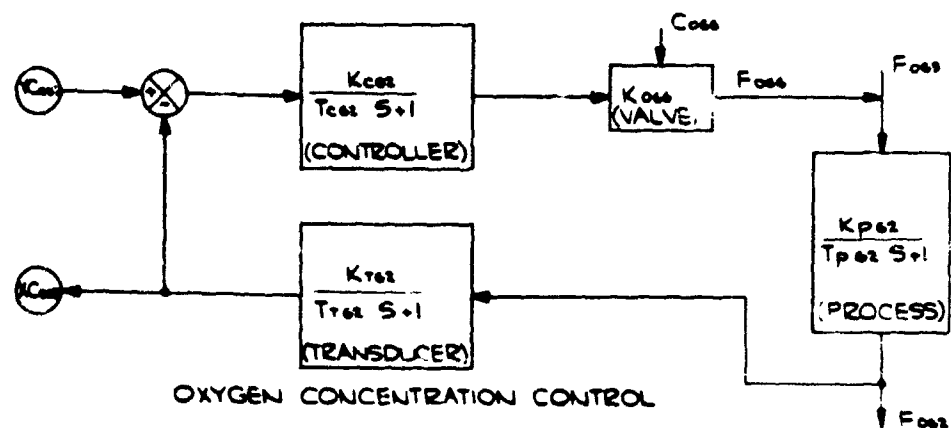
SALINITY CONCENTRATION CONTROL



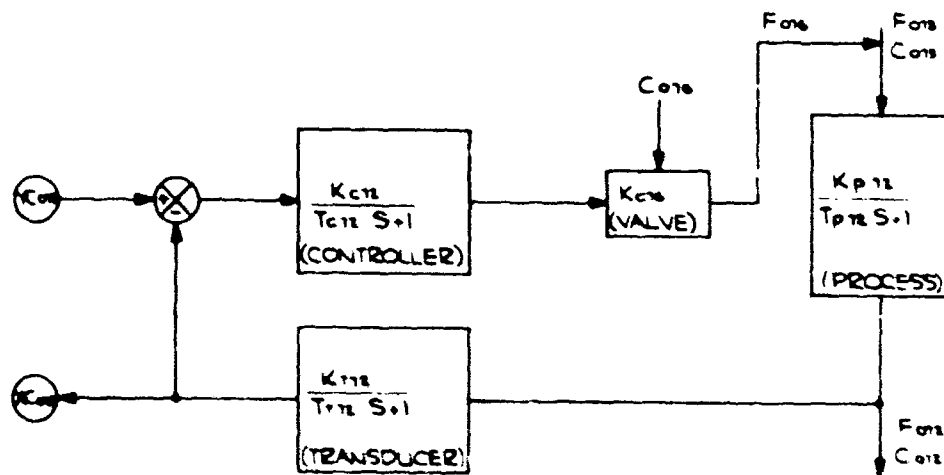
ALKALINITY CONCENTRATION CONTROL AND ALKALINITY CORRECTION

LEGEND:
 K - GAIN
 T - TIME CONSTANT
 F - FLOW
 C - CONCENTRATION
 X - ELECTRICAL SIGNAL
 Y - REFERENCE
 S - LAPLACE OPERATOR

OF THE ANALOG CONTROLLERS



OXYGEN CONCENTRATION CONTROL



H₂S CONCENTRATION CONTROL

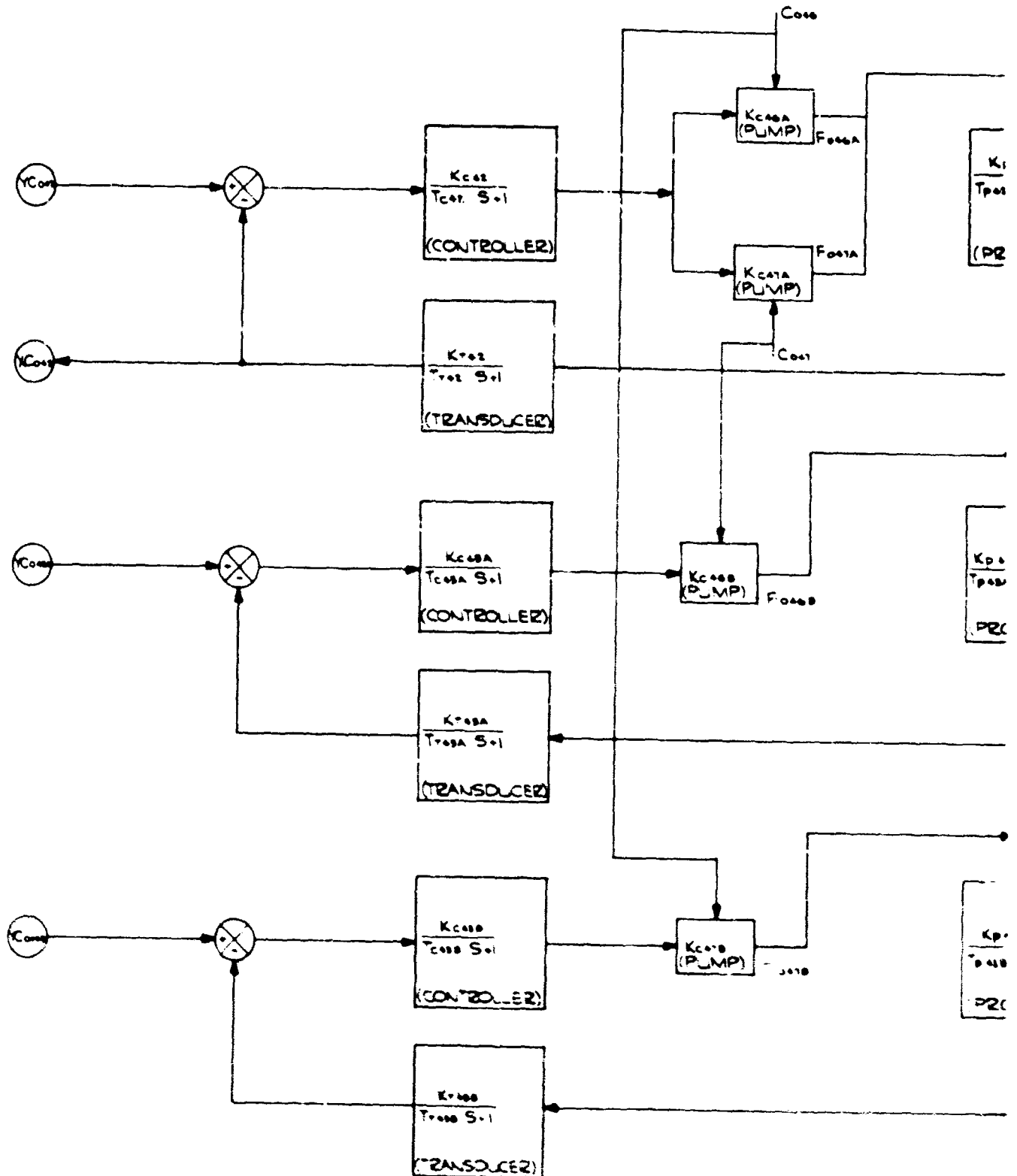
LEGEND:

- K • GAIN
- T • TIME CONSTANT
- F • FLOW
- C • CONCENTRATION
- X • ELECTRICAL SIGNAL TO COMPUTER
- Y • REFERENCE SIGNAL FROM COMPUTER
- S • LAPLACE OPERATOR

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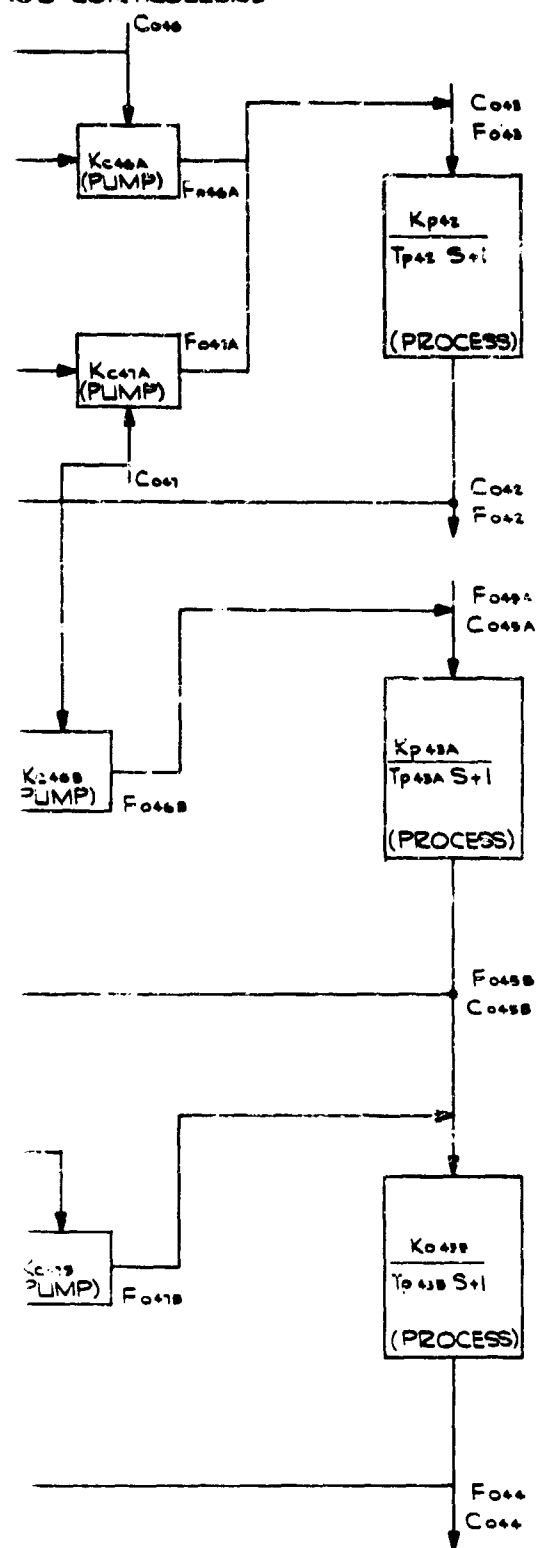
Figure 11

BLOCK DIAGRAMS OF THE ANALOG CONTROLLERS



PH CONCENTRATION CONTROL AND ALKALINITY STRIP

OG CONTROLLERS



LEGEND:

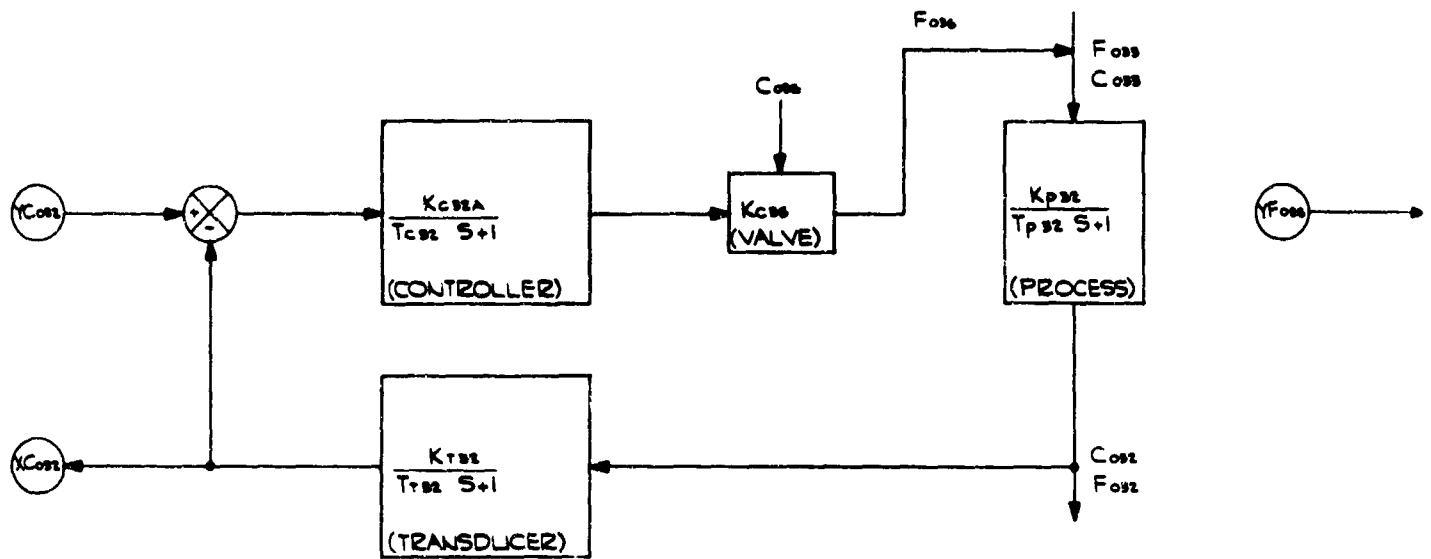
- K • GAIN
- T • TIME CONSTANT
- F • FLOW
- C • CONCENTRATION
- X • ELECTRICAL SIGNAL TO COMPUTER
- Y • REFERENCE SIGNAL FROM COMPUTER
- S • LAPLACE OPERATOR

RIP

| | |
|-------|--------|
| 70143 | 099562 |
| DATE | NOV 67 |

Figure 12

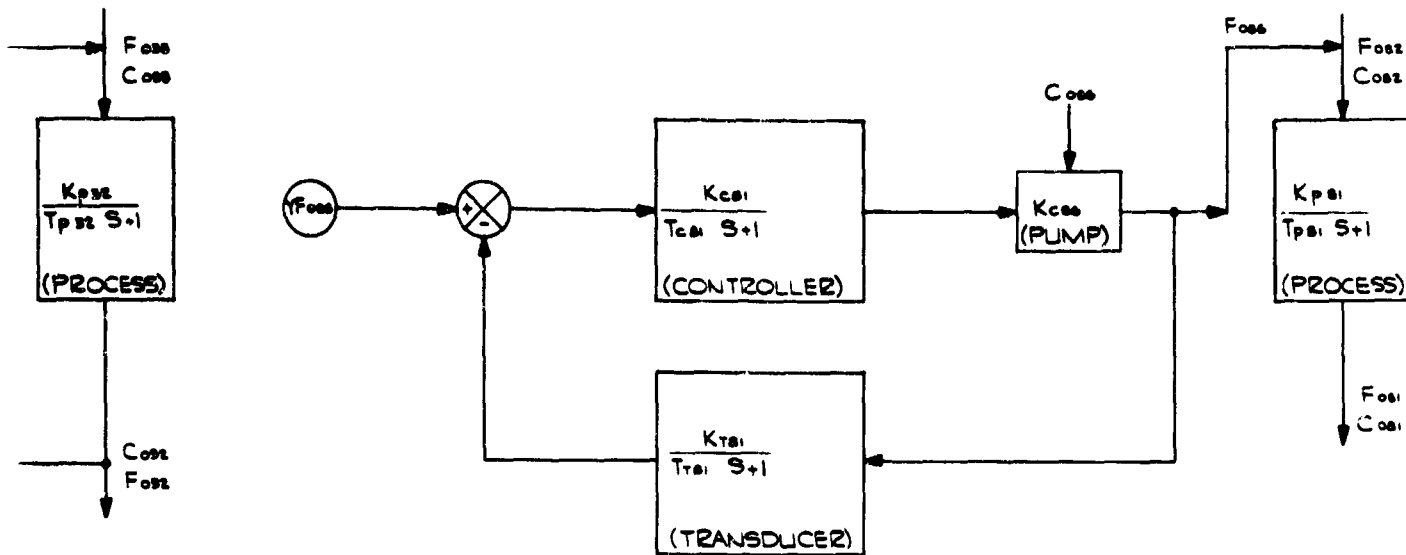
BLOCK DIAGRAMS OF THE ANALOG CON-



CO₂ CONCENTRATION CONTROL

A

GRAMS OF THE ANALOG CONTROLLERS



PO4 FLOW CONTROL

LEGEND:

- K • GAIN
- T • TIME CONSTANT
- F • FLOW
- C • CONCENTRATION
- X • ELECTRICAL SIGNAL TO COMPUTER
- Y • REFERENCE SIGNAL FROM COMPUTER
- S • LAPLACE OPERATOR

APPENDIX



AEROJET-GENERAL CORPORATION

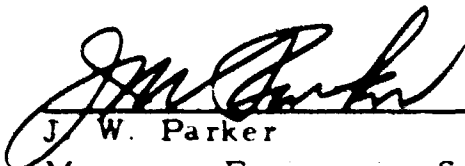
CODE IDENT. NO. 70143

SPECIFICATION AGC-10545

SIMULATOR, SEA WATER

| | | | | | | |
|--|-----------------|--------------|--|--------------|--|-------------------|
| SUPERSEDING: | | | | | | |
| AGC- DATE | | AGC- DATE | | AGC- DATE | | |
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AGC-10545

SPECIFICATION
(PRELIMINARY)
SIMULATOR, SEA WATER

1. SCOPE

1.1 Scope. - Developmental experiments at the U. S. Naval Civil Engineering Laboratory require the conversion of surface sea water to sea water whose physical and chemical parameters approach those found at different depths in the ocean. This specification covers the requirements for a Sea Water Simulator to analyze and control certain chemical parameters of a sea water stream to provide a one gallon per minute output of sea water having the desired composition.

2. APPLICABLE DOCUMENTS

2.1 The following documents of the issue in effect on the date of invitation for bids, form a part of this specification to the extent specified herein.

STANDARDS

Military

MS 33586

Metals, Definition of Dissimilar

(Copies of documents required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

DRAWINGS

AGC 099562

Sea Water Simulator

PUBLICATION

Report No. CR 67.004

Monitoring and Control of
Sea Water Composition

3. REQUIREMENTS

3.1 General requirements. - The Sea Water Simulator shall provide for the compositional analysis and control of a stream of sea water with respect to the eight chemical parameters discussed in paragraph 3.2. It shall be capable of being operated by any qualified engineering technician after an initial training period. The simulator shall be capable of continuous operation for durations of up to six months based on the availability of a technician for occasional periodic maintenance adjustment eight hours per day five days per week, Monday through Friday; the simulator must be capable of automatic, completely unattended operation throughout other periods.

3.2 Performance characteristics. - The simulator shall provide for the analysis of the eight chemical parameters and within the ranges indicated in Table 1. With the exception of E_h which will not be controlled, the chemical parameters shall be controlled so that an output flow of one gpm will have a specific composition within the limits of accuracy indicated in Table 1. Appropriate corrections or compensations shall be provided so that sea water, when adjusted at the temperature and pressure in the simulator will have a desired composition for use in a test system that may be operated at temperatures from zero to 20 deg C, and at pressures from zero to 20,000 psi. It should be understood that chemical interactions and physical effects may occur as a result of this transition, and that the arbitrary selection of certain limiting values within the control ranges may result in incompatible situations, as indicated in paragraph III of Report No. CR 67.004.

3.3 Design. - The design is contained in AGC Drawing No. 099562. The simulator is designed to provide a continuous stream of controlled-composition sea water at a flow of one gpm. The majority of adjustments are made within a closed loop portion of the simulator. Before entering the closed loop, sea water is filtered, pretreated to remove carbonate alkalinity if this is greater in the incoming sea water than is desired in the output stream, and adjusted to some desired pH value. This preadjusted sea water is used to feed the closed loop of the simulator at a required rate for the duration of the test period. Within the closed loop the sea water stream is maintained at zero to one deg C, and at zero to 15 psig and is circulated at a rate of 20 gpm. Solutions are metered into this circulating sea water stream to adjust the salinity, pH, and alkalinity. The sea water is then passed through a mixing column in which the sea water is equilibrated with a gas mixture to add or remove carbon dioxide, oxygen, and hydrogen sulfide as required in maintaining the composition. Beyond these addition points the stream is analyzed by means of chemical transducers, from which signals are derived to control the rate at which reagents are added. Between the chemical transducers and the points of further sea water addition, a one-gpm stream of sea water is drawn off for final adjustments for alkalinity and phosphate and is conveyed to a heat exchanger and then to the point of use.

TABLE 1

| <u>Chemical Parameter</u> | <u>Range</u> | <u>Accuracy</u> |
|------------------------------------|-----------------|-----------------|
| Salinity, ppt | 33.0 to 35.0 | 0.035 |
| Alkalinity, meq/l | 0.5 to 3.0 | 0.10 |
| Dissolved free carbon dioxide, ppm | 0 to 50 | 1.0 |
| pH | 6.0 to 9.0 | 0.03 |
| E _h , mv | +1400 to -1400 | 10 |
| Dissolved oxygen, ml/l | 0 to saturation | 0.15 |
| Dissolved hydrogen sulfide, ppm | 0 to 50 | 3.0 |
| Phosphate, ppm | 0 to 100 | 3.0 |

Because of the interaction of certain physical and chemical parameters, it is necessary in many cases for the rates of reagent additions to be computed to compensate for differences in the conditions prevailing in the loop and those employed at the point of use. This necessitates that transducer and set point values be fed into a computer/controller so that a corrected control signal can be calculated and directed to the appropriate metering device.

3.4 Materials of construction. -

3.4.1 Materials contacting the sea water stream. - The selection of materials shall be guided by the need to avoid heavy metal ion contamination of the sea water stream. The concentrations of such ions added to the uncontaminated sea water stream under normal operating conditions shall not exceed:

| | |
|-----------|----------|
| Copper | 1 ppm |
| Lead | 1 ppm |
| Iron | 5 ppm |
| Nickel | 1 ppm |
| Mercury | 0.05 ppm |
| Vanadium | 0.5 ppm |
| Manganese | 1 ppm |

3.4.1.1 Non-metals. - The preferred materials for all parts contacting the sea water stream are halogenated, unplasticized polymers having low moisture absorption and cold flow characteristics.

3.4.1.2 Metals. - Where the use of plastics is impossible or impractical, metals showing minimal corrosion in sea water, or glass or plastic coated metals shall be used. Titanium is the preferred metal for sea water service. Dissimilar metals shall not be used in intimate contact with each other. Dissimilar metals are defined in MS 33586.

3.4.2 Other components. - Mechanical components and surfaces that do not come into contact with the sea water stream shall be constructed of materials that will withstand occasional exposures to salt water, such as might occur because of leakage or spillage. Electrical and electronic devices forming a part of the simulator shall be suitably protected or isolated.

3.5 Components. - Sheet 2 of Drawing No. 099562 lists the mechanical equipment required in the construction of the simulator. These components together with the necessary piping, the computer/controller, and the transducers shall comprise the components of the Sea Water Simulator.

3.6 Details of components. - The types of components required in the construction of the Sea Water Simulator are listed below. This listing also gives the number of each required and references the paragraph of this specification where detailed descriptions may be found.

| <u>Component</u> | <u>Number Required</u> | <u>Paragraph</u> |
|----------------------|------------------------|------------------|
| Tank | 15 | 3.6.1 |
| Pump | 13 | 3.6.2 |
| Mixing Column | 1 | 3.6.3 |
| Filter | 4 | 3.6.4 |
| Eductor | 1 | 3.6.5 |
| Heat Exchanger | 5 | 3.6.6 |
| Refrigeration System | 1 | 3.6.7 |
| Valve | 19 | 3.6.8 |
| Computer/Controller | 1 | 3.6.9 |
| Transducer | 33 | 3.6.10 |

3.6.1 Tanks. - The tanks T-1 through T-15 shall meet the requirements given below and in Table 2.

3.6.1.1 Materials of construction. - Tanks T-1, T-2, T-3, T-4, T-5, T-7, T-8, T-10, T-11, T-13, T-14, and T-15 shall be constructed of rigid polyvinyl chloride, or polyethylene, or an equivalent, sea-water compatible plastic. Tanks T-6 and T-12 shall be constructed of rigid polyvinyl chloride or of fiberglass-reinforced bisphenol-A, polyester resin, or epoxy resin. Tank T-9 shall be constructed of AISI Type 304 stainless steel.

3.6.1.2 Support. - All the tanks except T-9 shall be self-supporting or shall be provided with a steel cradle frame to support the tank when filled with water.

3.6.1.3 Working pressure. - All tanks will be used at atmospheric pressure except for T-9, which will operate at 50 psig.

3.6.1.4 Other requirements. - See Table 2 for working capacity, size, connections, and special instructions.

3.6.2 Pumps. - The pumps P-1 through P-13 shall meet the requirements given in Table 3.

3.6.3 Mixing column. - The mixing column M-1 shall have the characteristics described here or equivalent.

3.6.3.1 Design. - It will be a counter-current mixer consisting of ten 3-in. high stages separated by horizontal baffles. The turbine shaft will pass through a center hole in each horizontal baffle. Each stage will contain a 2-in. diameter turbine. Vertical baffles will be located in the periphery of each stage to create turbulence. The turbine shaft will be driven with a variable-speed, one-half

TABLE 2
PRELIMINARY TANK SPECIFICATIONS

| | <u>T-1</u> | <u>T-2</u> | <u>T-3</u> | <u>T-4</u> | <u>T-5</u> | <u>T-6</u> | <u>T-7</u> | <u>T-8</u> | <u>T-9</u> | <u>T-10</u> | <u>T-11</u> | <u>T-12</u> | <u>T-13</u> | <u>T-14</u> | <u>T-15</u> |
|-------------------------------------|--|--|----------------|----------------|--------------------------------|-------------------------|----------------|----------------|---|----------------|----------------|--|----------------|----------------|---|
| Working capacity; gal. | 50 | 50 | 50 | 50 | 200 | 500 | 75 | 75 | 3 | 50 | 50 | 500 | 75 | 75 | 50 |
| Dimensions, ft; dia., height | 2, 3 | 2, 3 | 2, 3 | 2, 3 | stan- dard | stan- dard | 2-1/2, 3 | 2-1/2, 3 | 1/3, 3 | 2, 3 | 2, 3 | stan- dard | 2-1/2, 3 | 2-1/2, 3 | 2, 3 |
| Connections: location; dia., in. | lid, 1/4 lid, 3/4 bottom, 1/2 level, 3/4 level, 3/4 behind weir, 3/4 | lid, 1/4 side, 3/4 bottom, behind weir, 3/4 | bottom, 1/2 | bottom, 1/2 | in, 1-1/2 bottom, 3/4 | in, 2 bottom, 3/4 | bottom, 1/2 | bottom, 1/2 | bottom, 1 gas out- let, 1/2 water in- let, 1/2 drain, 1/2 bleed, 1/2 | bottom, 1/2 | bottom, 1/2 | in, 2 bottom, 3/4 mixer port, 6 hand- hole, 12 | bottom, 1/2 | bottom, 1/2 | outlet, 1/2 lid, 1/2 drain, 1/2 |
| Notes | 1, 2, 3, 4, 5 | 1, 2, 3, 4, 5 | 1, 2, 3 | 1, 2, 3 | 1, 6, 7, 8 | 1, 6, 7, 8 | 1, 2, 3 | 1, 2, 3 | 9 | 1, 2, 3, 5 | 1, 2, 3, 5 | 1, 5, 6, 7, 8 | 1, 2, 3, 5 | 1, 2, 3, 5 | 1, 2, 3, 5, 10 |

Notes:

1. Vertical
2. Dished bottom
3. Removable lid
4. Vertical weir
5. With mixer
6. Flat bottom
7. Flat or dished top
8. Closed
9. Schedule 10 pipe, bottom capped, with sparger, flanged top
10. With sight glass

TABLE 3
PRELIMINARY PUMP SPECIFICATIONS

[illegible]

NOTES: 1. To include injection nozzle and anti-siphon or back-pressure valve.

2. Automatic adjustment from zero to full capacity by controlling stroke length or drive speed. Actuated by low-level electric signal from controller.

horsepower motor. The column will be provided with liquid inlet and gas outlet at both top and bottom. The column will be approximately 6 in. in diameter and approximately 4-ft. high (6-ft overall).

3.6.3.2 Material of construction. - The column will be of Pyrex glass. The internal parts will be of titanium.

3.6.4 Filters. - The filters F-1 and F-2 shall meet the requirements set forth below when operated at ambient temperatures.

3.6.4.1 Materials of construction. - The preferred materials of construction are polyvinyl chloride, polypropylene, or polyethylene, or other non-metallics which are corrosion-resistant in sea water service.

3.6.4.2 Pressure characteristics. -

3.6.4.2.1 Pressure rating. - The minimum pressure rating shall be 50 psig.

3.6.4.2.2 Pressure drop. - The normal pressure drop shall not exceed one psi and the maximum pressure drop with cartridge loaded shall not exceed 10 psi.

3.6.4.3 Porosity. -

3.6.4.3.1 Prefilters, F-1. - The porosity will be recommended by manufacturer to permit optimum performance of filters, F-2.

3.6.4.3.2 Filters, F-2. - The pore size will be 0.25 microns rated for 99.99 percent removal of 0.45-micron particles and 100 percent removal of 0.8-micron particles. The filter will deliver clear sea water with an average removal of not less than 99.999 percent of incident bacteria.

3.6.4.4 Capacity. - The filter system F-1 and F-2 shall have the capacity to operate continuously at a one-gpm flow rate meeting the requirements of paragraphs 3.6.4.2 and 3.6.4.3 without attention, cleaning, or filter replacement for at least 72 hours.

3.6.4.5 Servicing. - The design of the filter housing shall provide easy access for cleaning, replacement of filter cartridge, and other maintenance requirements.

3.6.5 Eductor. - The eductor shall meet the requirements set forth below.

3.6.5.1 Materials of construction. - The eductor shall be constructed of a compatible plastic such as polyvinyl chloride, polypropylene, or polyethylene.

3.6.5.2 Operating conditions. - The eductor shall be suitable for continuous service at a temperature of zero deg C and a minimum pressure of 100 psig.

3.6.5.3 Characteristics. - The eductor shall be capable of providing intimate mixing of a one-gpm sea water stream delivered at 20 to 25 psig with two miscible aqueous streams delivered at flow rates of up to 0.20 gph and at pressures up to 50 psig.

3.6.6 Heat exchangers. - The heat exchangers E-1 through E-4, and E-5 shall have the characteristics indicated below and in Table 4.

TABLE 4
PRELIMINARY HEAT EXCHANGER SPECIFICATIONS

| | <u>E-1</u> | <u>E-2</u> | <u>E-3</u> | <u>E-4</u> | <u>E-5</u> |
|----------------------------------|------------|------------|------------|------------|------------|
| Sea water flow rate; gpm | 1 | 20 | 20 | 20 | 1 |
| Input temperature; ambient deg C | | 0-2 | 0-2 | ambient | 0-1 |
| Output temperature; deg C | 0-2 | 0-1 | 0-1 | 0-1 | 0-20 |
| Pressure rating; min, psig | 50 | 50 | 50 | 50 | 50 |
| Pressure drop; max, psi | 5 | 5 | 5 | 5 | 5 |

3.6.6.1 Material. - The preferred material for heat exchange is Teflon or graphite. Titanium is also acceptable.

3.6.6.2 Coolant. - The coolant may be any fluid that allows the requirements of Table 4 and of paragraph 3.6.7 to be met.

3.6.6.3 Type. - The heat exchangers shall be saturation-type exchangers with an exchange capacity and efficiency such that the temperature of the sea water stream approaches to within 0.5 deg C of the coolant temperature in traversing 70 percent of the exchanger tube length.

3.6.7 Refrigeration system. - The refrigeration system R-1 shall have the cooling capacity to maintain the temperature conditions of E-1, E-2, E-3, and E-4 as specified in Table 4. This will assume the flow rates given in paragraph 3.6.6 and be based upon a specific heat for sea water of 4.2 absolute joules per gram of sea water. The coolant temperature shall be maintained within the range

from zero to one deg C. The refrigeration system shall not be required to maintain the conditions for E-5; temperature control for the latter will be available from existing devices at the U.S. Naval Civil Engineering Laboratory.

3.6.8 Valves. - The automatic and manual valves, CV-1 through CV-8 and V-1 through V-19, respectively, shall meet the minimal requirements given below.

3.6.8.1 Automatic valves. - The valves shall be constructed of compatible plastic or metal and shall be supplied with a pneumatic or electric controller that will be actuated and controlled by a low-level electric signal. Additional requirements are given in Table 5.

TABLE 5

PRELIMINARY SPECIFICATION FOR AUTOMATIC VALVES

| | <u>CV-1</u> | <u>CV-2</u> | <u>CV-3</u> | <u>CV-4</u> | <u>CV-5</u> | <u>CV-6</u> | <u>CV-7</u> | <u>CV-8</u> |
|----------------------------------|-------------|-------------|----------------|-------------|-------------|-------------|-------------|-------------|
| Size; in. | 3/4 | 3/4 | as required | 1/2 | 1/4 | 1/4 | 1/4 | 1/4 |
| Service | ← liquid → | | | | ← gas → | | | |
| Fluid flow max, gpm | 2 | 2 | as required | 1 | 0.5 | 0.25 | 0.25 | 0.025 |
| Fluid tem- perature, deg C | ambient | | 0 | 0 | ← ambient → | | | |

3.6.8.2 Manual valves. - These valves shall be constructed of compatible plastic or metal and shall meet the additional requirements given in Table 6.

3.6.9 Computer/Controller. - The function of the computer/controller is to receive transducer signals, to amplify the signals to the proper level, to compute from appropriate set point and transducer signals the control signal, to generate a reference signal by comparing the control and transducer signals. It shall accomplish the control functions shown and described on Sheets 6, 7, 8, and 9 of Drawing No. 099562 so as to provide the accuracies specified in paragraph 3.2. The requirements listed below are suggested requirements for the components of the computer/controller.

TABLE 6
PRELIMINARY SPECIFICATIONS FOR MANUAL VALVES

| | <u>V-1</u> | <u>V-2</u> | <u>V-3</u> | <u>V-4</u> | <u>V-5</u> | <u>V-6</u> | <u>V-7</u> | <u>V-8</u> | <u>V-9</u> | <u>V-10</u> |
|---------------------------|---|---|------------|------------|------------|------------|------------|------------|------------|---|
| Number of ways | 2 | 2 | 2 | 2 | 4 | 4 | 2 | 3 | 2 | 2 |
| Size, in. | 3/4 | 3/4 | 3/4 | 3/4 | 1-1/2 | 1-1/2 | 1-1/2 | 1/4 | 1/4 | 1/4 |
| Service | <div> <div>←</div> <div>sea water</div> <div>→</div> </div> | | | | | | | | | |
| Fluid flow rate; max, gpm | 2 | 2 | 2 | 2 | 20 | 20 | 20 | 1 | 1 | .01 |
| Fluid temperature; deg C | ← | <div> <div>←</div> <div>ambient</div> <div>→</div> </div> | | | | 0 | 0 | 0 | ← | <div> <div>←</div> <div>ambient</div> <div>→</div> </div> |
| | | | | | | | | gas | gas | Na ₂ HPO ₄ solution |

TABLE 6 (Continued)

| | <u>V-11</u> | <u>V-12</u> | <u>V-13</u> | <u>V-14</u> | <u>V-15</u> | <u>V-16</u> | <u>V-17</u> | <u>V-18</u> | <u>V-19</u> |
|---------------------------|--------------------------------|----------------|--------------------|------------------|-----------------|---------------|-------------|-------------|-------------|
| Number of ways | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| Size; in. | 1/4 | 1/4 | 1/4 | 1/4 | 1/4 | 3/4 | 3/4 | 1-1/2 | 1-1/2 |
| Service | NaHCO ₃ solution | dist. water | conc. sea water | NaOH solution | HCl solution | ← sea water → | | | |
| Fluid flow rate; max, gpm | .02 | .12 | .12 | .006 | .006 | 2 | 2 | 20 | 20 |
| Fluid temperature; deg C | ← ambient → | | | | → 0 → | | | | |

3.6.9.1 Signal amplification. - The amplifiers will amplify the transducer signals from the output levels noted in 3.6.10 to some convenient standard value such as zero to 10 v. The long-term gain accuracy shall be ± 0.01 percent in an operating temperature range of 20 to 40 deg C. The input and output impedances shall be compatible with the transducers and the multiplexing device.

3.6.9.2 Input and output multiplexers. - The input and output multiplexers shall each be capable of scanning 20 points per second. Each shall be capable of random programming.

3.6.9.3 Analog-to-digital converter. - The analog-to-digital converter shall have a conversion time of less than one millisecond. It shall give a conversion accuracy of 0.01 percent per year while operating at 20 to 40 deg C. The output and the word format shall be compatible with the computer and with the digital-to-analog converter.

3.6.9.4 Digital computer. - The digital computer shall have the memory capacity to store the program and data input and to perform the calculations indicated in Sheets 8 and 9 of the Drawing No. 099562. It shall provide a calculation accuracy of 0.01 percent. The computer speed shall be adequate to meet the time requirements specified for signal updating at the analog hold circuits.

3.6.9.5 Input to computer. - The method and devices for putting programs and data into the computer may be any commercial approach such as punched card, punched paper tape, typewriter, etc. Factors of primary consideration will be low cost and ease of operation by laboratory personnel.

3.6.9.6 Printout. - The printed record may be a typewriter, teletypewriter, or other common commercial devices. It shall be capable of printing out a complete record of simulator parameters and concentrations in five minutes at 30-minute intervals.

3.6.9.7 Digital-to-analog converter. - The digital-to-analog converter shall have a conversion time of less than one millisecond. It shall give a long-term conversion accuracy of 0.01 percent per year. It shall be compatible with the output and word format of the analog-to-digital converter and the digital computer. Its analog output shall be compatible with the input to the analog-to-digital converter and with the output multiplexer.

3.6.9.8 Analog hold circuits. - The analog hold circuits shall provide reference signal accuracies of 0.10 percent compared to those of the computer output based upon the signals being updated once each second. The hold circuits shall operate over the voltage range selected for the output of the digital-to-analog converter.

3.6.9.9 Analog controllers. - The analog controllers will receive and compare the transducer signals with the computer reference signal to generate the appropriate error signals (electric or pneumatic) necessary to control the appropriate valves or metering pumps. The accuracy shall be 3 percent or less.

3.6.9.10 Transducers. - The transducers used in the construction of the Sea Water Simulator shall have characteristics equivalent to or better than those given in Table 7. In-line devices shall be used wherever possible. These devices shall be constructed of compatible non-metals wherever possible.

3.7 Selection of specifications and standards. - The components used in the fabrication of the simulator shall, insofar as possible, be commercial parts. If it becomes necessary to modify commercial parts or to manufacture special parts, the work shall be in accordance with commercial standards.

3.8 Maintainability. - The arrangement of components shall be such as to provide easy access for maintenance, repair, removal, replacement, and calibration of parts requiring attention, such as transducers, valve controllers, metering pumps, filters, etc. The insulation on insulated portions of the loop shall have joints or break points to facilitate the removal and replacement of parts.

3.9 Measurements. - The dimensions and weight of the Sea Water Simulator shall be a minimum commensurate with design characteristics given in paragraph 3.3 and in Drawing No. 099562 and the maintainability constraints given in paragraph 3.8.

3.10 Finish. - Commercial parts may be used with the original standard commercial finish. Altered or fabricated parts shall be touched up, finished, or refinished in accordance with standard commercial practice. Insulated parts shall have no special finish over the insulation. Corrosion-resistant coatings shall be applied only to metal surfaces outside the treatment loop that are not inherently corrosion resistant and that may be expected to be exposed to sea water in case of leakage or spillage.

3.11 Identification of product. - The simulator shall be labeled with a metal or durable plastic nameplate containing the following information:

SEA WATER SIMULATOR
CONTRACT NO. _____

If in the construction it is necessary to assemble the simulator in two or more physically separate cabinets or chassis, each shall be labeled as above except that each unit tag shall also contain a descriptive phrase (such as LOOP, COMPUTER/CONTROLLER) between "Sea Water Simulator" and "Contract No. _____" to indicate its use or function. Identifying tags shall be placed in

TABLE 7
PRELIMINARY TRANSDUCER SPECIFICATIONS

| | AT-1 (Salinity) | AT-2 (Alkalinity) | AT-3 (CO ₂) | AT-4 (pH) | AT-5 (E _N) | AT-6 (O ₂) | AT-7 (H ₂ S) | AT-8 (Phosphate) | AT-10 (pH) |
|-------------------------------|--------------------|----------------------|----------------------------|--------------|---------------------------|---------------------------|----------------------------|---------------------|---------------|
| Range | 32.5-36.0 ppt | 0.5 - 3.0 meq/l | 0 - 50 ppm | 6 - 9 pH | +1400 to -1400 mv | 0 - 10 ml/l | 0 - 50 ppm | 0 - 100 ppm | 2 - 10 pH |
| Accuracy | .03 ppt | .06 meq/l | 0.5 ppm | .02 pH | 10 mv | 0.1 ml/l | 2.5 ppm | 2 ppm | .1 pH |
| Calibration interval; days | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 4 | 180 |
| Response time; max | 1 sec | 3 min | 1 min | 10 sec | 10 sec | 10 sec | 1 min | 5 min | 10 sec |
| Output signal; mv | 0-10 mv | 0-10 mv | 0-10 mv | 0-10 mv | 0-10 mv | 0-10 mv | 0-10 mv | 0-10 mv | to AC10 |
| Readout | meter | meter | meter | meter | meter | meter | meter | meter | - |
| Type of fluid | liquid | liquid | liquid | liquid | liquid | liquid | liquid | liquid | liquid |
| Process temperature; deg C | 0 to 1 | 0, ambient | 0 to 1 | 0 to 1 | 0 to 1 | 0 to 1 | 0 to 1 | 0 to 1 | ambient |
| Process pressure; psig | <50 | <50 | <50 | <50 | <50 | <50 | <50 | <50 | <50 |
| Flow rate | 20 gpm | 20 gpm | 20 gpm | 20 gpm | 20 gpm | 20 gpm | 20 gpm | 20 gpm | 1 gpm |
| Line size; in. | 1-1/2 | 1-1/2 | 1-1/2 | 1-1/2 | 1-1/2 | 1-1/2 | 1-1/2 | 1-1/2 | 3/4 |
| Linear velocity; fpm | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 | 3.15 | 0.4 |
| Power | 110 V, 60 cps | | | | | | | | |
| Notes | 1 | 2 | | | | | | | |

- NOTES:**
1. When meter readout is indicated it will be remote, panel-mounted, and supplied with the transducer.
 2. Several transducers such as AT-2, AT-3, AT-7, AT-8, and AT-12 will probably require sampling tees for sampling.
 3. This analyzer is the same as AT-2. One device will be time-shared to accomplish these analyses.

TABLE 7 (Continued)

| | AT-11 (pH) | AT-12 (Alkalinity) | TT-1 | TT-2 | TT-3 | TT-4 | TT-5 | PT-1 | PT-2 |
|----------------------------|------------------|-----------------------|---------------|-------------|-----------|-------------|-------------|--------------|-----------|
| Range | 2-10 pH | | 0-50 deg C | 0-5 deg C | 0-5 deg C | 0-25 deg C | 0-5 deg C | 0-100 psig | 0-50 psig |
| Accuracy | .1 pH | | 1 deg C | 0.002 deg C | 0.5 deg C | 0.002 deg C | 0.002 deg C | 5 psi | 1 psi |
| Calibration interval; days | 180 | | 30 | 30 | 30 | 7 | 7 | 180 | 7 |
| Response time; max | 10 sec | | 1 sec | 1 sec | 1 sec | 1 sec | 1 sec | 1 sec | 1 sec |
| Output signal; mv | to AC11 | | to meter | to meter | to meter | 0-10 mv | to meter | to alarm | 0-10 mv |
| Readout | - | | meter | meter | meter | meter | meter | visual-alarm | meter |
| Type of fluid | liquid | | liquid | liquid | liquid | liquid | liquid | liquid | liquid |
| Process temperature; deg C | ambient | | 0 to 2 | 0 to 2 | 0 to 2 | 0 to 20 | 0 to 5 | 0 to 30 | 0 to 5 |
| Process pressure; psig | < 50 | | < 50 | < 50 | < 50 | < 50 | < 50 | < 100 | < 50 |
| Flow rate | 1 gpm | | 20 gpm | - | - | 1 gpm | 20 gpm | 1 gpm | 20 gpm |
| Line size; in. | 3/4 | | 1-1/2 | tank | tank | 3/4 | 1-1/2 | 3/4 | 1-1/2 |
| Linear velocity; fpe | 0.6 | | 3.15 | - | - | 0.6 | 3.15 | 0.6 | 3.15 |
| Power | 110 V, 60 cps | | 110 V, 60 cps | | | | | | |
| Notes | | | | | | | | | |

(Table 7 concluded on Page 3)

a conspicuous location but so as not to interfere with the operation of the simulator. The tags shall be lettered legibly and shall be, or shall be coated with, non-corroding material to maintain legibility. Identifying tags, marks, or codes on individual components shall not be altered, defaced, or removed in the construction of the simulator, except they may be coated with a transparent coating to provide corrosion resistance.

3.12 Workmanship. - The Sea Water Simulator, including all parts and accessories, shall be fabricated and finished in a workmanlike manner.

4. QUALITY ASSURANCE PROVISIONS

4.1 Quality control and inspection. - The quality control and inspection system of the contractor shall be such as to assure the delivery of components of good commercial quality and workmanship. The prime contractor shall be responsible to see that the inspection is completed satisfactorily, whether in his own shop or by a subcontractor. This shall in no way relieve subcontractors of their responsibilities.

5. PREPARATION FOR DELIVERY

5.1 Packing and packaging. - The simulator and sub-assemblies shall be preserved, packaged, and packed in accordance with the contractor's best commercial practice in order to assure safe arrival at destination and be acceptable to common carriers.

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AEROJET-GENERAL CORPORATION

Plant: Azusa

Address: 1100 W. Hollyvale St., Azusa

Organization: Engineering Services Dept.

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DOCUMENT TITLE: **Simulator, Sea Water**

DOCUMENT NUMBER: **AGC-10545**

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| | | | |
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| 1. ORIGINATING ACTIVITY (Corporate author) Aerojet-General Corporation Azusa, California | | 2a. REPORT SECURITY CLASSIFICATION Unclassified | |
| | | 2b. GROUP | |
| 3. REPORT TITLE MONITORING AND CONTROL OF SEA WATER COMPOSITION | | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Final Report for Period January 1966 through December 1966. | | | |
| 5. AUTHOR(S) (Last name, first name, initial) Edgington, H. C. | | | |
| 6. REPORT DATE February 1967 | | 7a. TOTAL NO. OF PAGES 84 | 7b. NO. OF REFS 17 |
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| 11. SUPPLEMENTARY NOTES | | 12. SPONSORING MILITARY ACTIVITY U. S. Naval Civil Engineering Laboratory Port Hueneme, California | |
| 13. ABSTRACT <p>This report describes the work carried out in the study and preliminary design of a Sea Water Simulator. The purpose of the device is to approximate for various locales and depths, the sea water chemistry represented by eight chemical parameters: salinity, alkalinity, carbon dioxide, pH, oxygen, hydrogen sulfide, phosphate, and E_h.</p> <p>A literature search was conducted to elucidate this chemistry and to obtain data quantitatively interrelating these chemical systems and their physical states. A survey was made to compare the characteristics of commercially available control instrumentation and transducers. Based upon the information gathered, a system was then designed. The envisioned system incorporates computer control of both closed-loop and open-loop chemistries. Predicted accuracies for output composition control are reconciled with suggested USNCEL performance specifications.</p> | | | |

| 14. KEY WORDS | LINK A | | LINK B | | LINK C | |
|----------------------------|--------|----|--------|----|--------|----|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| Sea water | | | | | | |
| Simulation | | | | | | |
| Salinity | | | | | | |
| Dissolved oxygen | | | | | | |
| pH | | | | | | |
| Dissolved carbon dioxide | | | | | | |
| Alkalinity | | | | | | |
| E _h | | | | | | |
| Dissolved hydrogen sulfide | | | | | | |
| Computer | | | | | | |
| Transducers | | | | | | |
| Materials | | | | | | |
| Phosphate | | | | | | |

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